U.S. DEPARTMENT OF COMMERCE

BUREAU OF STANDARDS JOURNAL OF RESEARCH

Vol. 12 JUNE 1934 No. 6

CONTENTS

RP.	TITLE AND AUTHOR	Page
685.	An absolute determination of the ampere. Harvey L. Curtis and Roger W. Curtis	665
686.	Calorimetric determination of the heats of combustion of ethane, propane, normal butane, and normal pentane. Frederick D. Rossini	735
687.	Study of the system CaO-SiO_2-H_2O at 30 C and of the reaction of water on the anhydrous calcium silicates. E. P. Flint and Lansing S. Wells	751
688.	Preece test (copper-sulphate dip) for zinc coatings. Edward C. Groesbeck and H. H. Walkup	785
689.	Iodine number of wool: A method for determining the action of various chemical reagents on wool and other proteins. Milton Harris, Harvey A. Neville, and William C. Fritz	803
690.	Properties of white Braille papers for Library of Congress publications. C. G. Weber	811
	Index to volume 12 (January to June 1934—Research Papers 630 to 690)	817

A monthly periodical of pure and applied science published by our National Government

BUREAU OF STANDARDS JOURNAL OF RESEARCH

¶The January 1934 issue of the Bureau of Standards Journal of Research began the twelfth semiannual volume of this periodical. The JOURNAL contains the Bureau's research papers and critical reviews in the fields of science and technology. ¶Fundamental researches always in progress in the Bureau's laboratories have their outlet in the Bureau of Standards Journal of Research. If you are interested in following the new developments in science and technology, you should receive the JOURNAL. If you are already a subscriber, continue your subscription; if not, you are invited and urged to send in your subscription at once.

TECHNICAL NEWS BULLETIN

¶This is a monthly publication containing short articles reporting progress of work in the Bureau's laboratories, abstracts of papers which appear in the Bureau of Standards Journal of Research, reports of scientific and technical meetings in which the Bureau has taken part, and a list of all publications by members of the staff, and other topics within the Bureau's fields. This publication is designed primarily to give its subscribers a general review of important and timely activities and accomplishments at the Bureau. The material is presented in brief, but adequate form, for the information of those who are interested in the general activities of the Bureau. It is a prompt and reliable source of official information. If you are not already a subscriber to this monthly periodical you are urged to place your subscription.

ANNUAL SUBSCRIPTION	Prices	
	United States, Canada, Cuba, Mexico, Newfoundland, Republic of Panama	Other countries
Bureau of Standards Journal of Research: [1]		
12 monthly issues (2 volumes), paper covers	$2.50	$3.25
Bound volume (½ year, 1 volume), blue buckram	3.00	3.50
Technical News Bulletin 12 monthly issues	.50	.70

[1] Research Papers, reprinted individual articles appearing in the Journal of Research, are available from the Superintendent of Documents shortly after the appearance of the monthly issue of the JOURNAL.

Address orders only to
Superintendent of Documents, Government Printing Office,
Washington, D.C.

U.S. DEPARTMENT OF COMMERCE
DANIEL C. ROPER, Secretary
BUREAU OF STANDARDS
LYMAN J. BRIGGS, Director

BUREAU OF STANDARDS JOURNAL OF RESEARCH

June 1934
Vol. 12, No. 6

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1934

For sale by the Superintendent of Documents, Washington, D.C. - - Price 25 cents; $2.50 per year on subscription

Beginning with the July 1934 issue the Journal will be continued under the new title Journal of Research of the National Bureau of Standards. Also beginning with the July 1934 issue of the Journal of Research of the National Bureau of Standards the prices of the separate Research Papers appearing in the monthly issues will be given on the front cover of the Journal.

This arrangement will provide a prompt and convenient method whereby readers of the Journal of Research desiring copies of separate Research Papers appearing therein may send their orders without delay to the Superintendent of Documents, United States Government Printing Office, Washington, D.C.

DEPOSITED BY THE
UNITED STATES OF AMERICA
JUL 5 '34

U.S. DEPARTMENT OF COMMERCE BUREAU OF STANDARDS

RESEARCH PAPER RP685

Part of Bureau of Standards Journal of Research, vol. 12, June 1934

AN ABSOLUTE DETERMINATION OF THE AMPERE

By Harvey L. Curtis and Roger W. Curtis

ABSTRACT

The current balance originally used by Rosa, Dorsey, and Miller in 1911 has been somewhat modified and used to determine the absolute value of the ampere. The value in absolute amperes of the current in the coils of the balance was determined from the measured constants of the coils and the electromagnetic force between them. The most important constant which could be directly measured was the ratio of the radii of the coils, which was measured by an electrical method. The values obtained on four sets of coils indicated that there was no error in the measurement of the ratio of the radii greater than three parts in a million.

The current through the balance was measured not only in absolute units but also in terms of the international units of electromotive force and resistance as maintained at the Bureau of Standards. The final result of measurements with four different coil combinations was:

1 B.S. International Ampere = 0.999928 Absolute Ampere

The authors estimate that this result differs from the true value by less than 20 parts in a million.

This result agrees within experimental error with that obtained in 1911, indicating that the unit of current as realized at the Bureau of Standards by standard cells and standard resistances has not changed appreciably since then.

CONTENTS

	Page
I. Introduction	666
1. Importance of a new absolute determination of the ampere	667
2. Relation of the present work to that of 1911	667
II. Description of the current balance	668
1. The balance	668
(a) Optical system	669
(b) Sensitivity of the balance	669
(c) The weights	670
(d) Procedure in making a weighing	671
2. Coils and their mountings	671
(a) The coils	671
(b) Coil mounting	673
(c) Cooling system	673
III. Electrical circuit of the current balance	674
1. Constancy of current	675
2. Measurement of the current in B.S. international amperes	675
3. Reversal of current in the fixed coils	677
4. Leads to the moving coil	677
5. Thermal electromotive forces	678
6. Insulation resistance	680
7. Electrostatic forces	680
8. Magnetic effect of leads	680

Page
IV. Computation of the maximum force for unit current 681
1. Maximum force between circular filaments 681
2. Maximum force between coaxial coils 684
3. Maximum force for three maladjusted coils 686
V. Determination of the ratio of the radii of the coils 689
1. Outline of method 690
2. Mounting of the coils 691
3. Magnetometer 691
4. Optical system 691
5. Electrical connections 692
6. Procedure in taking observations 694
7. Adjustment of the coils and magnet 694
8. Theory of the adjustment of the coils 699
9. Temperature coefficient of expansion 701
10. Load coefficient of expansion 702
11. Correction for the length of the magnet 705
12. Correction for the sectional dimensions of the coils 707
13. Effect of the leads 708
14. Sources of error 709
15. Results 710
VI. Experimental determination of the maximum force between the coils 712
1. Measurement of the force for a given arrangement of the coils 712
2. Adjustment of the coils 714
3. Sum of the forces 716
4. Difference of the forces 716
5. Sources of error and corrections 717
(a) Adjustment of the coils 717
(b) Sensitivity of the balance 717
(c) Weights and buoyancy correction 718
(d) Acceleration of gravity 718
(e) Correction for the temperature of the coils 719
(f) Correction for the electrical load on the coils 721
(g) Lead correction 721
(h) Changes in the rest point during a run 721
(i) Convection currents in the air 722
(j) Magnetic bodies 722
(1) Magnetic masses attached to the moving system 722
(2) Magnetic masses outside the balance 722
(3) Magnetic bodies as a part of the coils themselves 723
(k) External magnetic fields 723
(l) Correction for the finite cross-section of the coils 724
(m) Errors resulting from differences between the actual and the theoretical coils 725
(n) Predicted error in the absolute value of the current 726
VII. Value of a current in B.S. international amperes and in absolute amperes 726
VIII. Discussion of results 733

I. INTRODUCTION

A determination of the absolute value of the international ampere as maintained at the Bureau of Standards has been completed. The method was that used by Rosa, Dorsey, and Miller in 1911, and a large part of their apparatus was employed. This investigation was undertaken to ascertain whether there had been an important change in the unit of current since 1911, and to determine the amount by which the present international unit of current differs from the absolute unit. The determination has been carried through with the idea of obtaining a reliable result at as early a date as possible.

The absolute determination of current had its inception in the work of Gauss.[1] The tangent galvanometer[2] provided the first

[1] Gauss, Pogg. Ann., vol. 28, p. 241, 1833.
[2] Pouillet, Pogg. Ann., vol. 42, p. 281, 1837

method [3] for an absolute current determination and this suggested to Weber [4] a unified system of absolute electrical units. The current balance was first used by Cazin [5] and later made an instrument of precision by Rayleigh.[6] In only two previous determinations [7, 8] did the results have an accuracy [9] greater than one part in 10,000. This report gives the results of a third precise determination.

1. IMPORTANCE OF A NEW ABSOLUTE DETERMINATION OF THE AMPERE

The International Committee of Weights and Measures decided in 1928 to adopt the absolute electrical units and to base the value of working standards on the results of absolute determinations. The national laboratories were requested to complete as soon as possible the absolute determinations which they had planned. The results herein reported are a part of the contribution of the Bureau of Standards.

This determination also gives information concerning the constancy of our own standards. In the absolute determination of the ampere which was made at the Bureau of Standards in 1911, the results were expressed in terms of the units of resistance and electromotive force of this Bureau. These units have been maintained by means of groups of standard resistances and standard cells. Individual members of each group have changed relative to the mean by appreciable amounts so that some doubt exists as to the accuracy of maintenance of these units of resistance and electromotive force.[10] Hence an absolute determination gives information concerning the changes which may have taken place in the electrical units.

2. RELATION OF THE PRESENT WORK TO THAT OF 1911

The current balance used in 1911 was chosen for this investigation partly because a large part of the apparatus was already available. Another reason was the desirability of having the Bureau of Standards method sufficiently different from that in use at the National Physical Laboratory so that the same systematic errors will not enter in the determinations at the two laboratories. Only these two types of current balances have been so perfected that precise results can be obtained by their use. Extensive development work will be necessary before determinations by any other method [11] will have the same accuracy as those by these current balances.

In the preliminary determination of the present series, made in 1927, all of the available apparatus which was used in 1911 was again used although it was set up in a different laboratory. Later the apparatus was modified in many details. The results of all the measurements that have been made are herein reported.

[3] Weber, Deutscher Naturforscher Verein, Berichte, p. 154, 1841.
[4] Weber, Ann. der Phy. u. Chem., vol. 82, p. 337, 1851. Translated in Phil. Mag., series 4, vol. 22, p. 226 ff. and p. 261 ff. 1861.
[5] Cazin, Ann de Chimie et de Physique, series 4, vol. 1, p. 257, 1864.
[6] Rayleigh, B. A. Report p. 445, 1882. Proc. Camb. Phil. Soc., vol. 5, p. 50. Phil. Trans. 175, p. 411, 1884.
[7] Ayrton, Mather and Smith, Roy. Soc., Phil. Trans. vol. 207A, p. 463, 1908.
[8] Rosa, Dorsey, and Miller, B.S. Bull., vol. 8, p. 269, 1911.
[9] The most recent determination was that of Shaw, but the accuracy of the results obtained did not exceed one part in 10,000. Roy. Soc., Phil. Trans. vol. 214A, p. 147, 1914.
[10] H. L. Curtis, The Establishment and Maintenance of the Electrical Units, Bull. National Research Council no. 93, p. 80, 1933.
[11] Some progress has been made by the authors towards the construction of an electrodynamometer of the Pellat type. Pellat, Bull. de la Soc. Internat. des Electriciens, series 2, vol. 8, p. 573, 1908. The mathematical theory has been developed by Snow, B.S. Jour. Research, vol. 1 (RP24), p. 685, 1928.

The current balance was of the Rayleigh type having a moving coil which was suspended with its plane horizontal from 1 of the pans of a balance, and 2 fixed coils which were placed, one above and the other below, the moving coil. Each of the coils had a square cross section, the linear dimensions of which were small as compared to the radius of the coil. The coils were horizontal and coaxial, and the fixed coils were at such a distance from the moving coil that the electromagnetic force on the latter was a maximum.

In order to determine in absolute measure the current in the coils, it was necessary to measure not only the electro-magnetic force on the moving coil but also the ratio of the effective radii of the coils, and to know the number of turns in each of the coils. The experimental work, therefore, consisted of two distinct parts; one, the determination of the ratio of the radii of the coils used; and second, the determination of the force between the coils produced by the current which was to be measured.

II. DESCRIPTION OF THE CURRENT BALANCE

The current balance and accessories were installed in basement rooms in the electrical building, the balance room having only two small outside windows with light-tight shutters. The temperature change of the balance room was often as small as 0.2° C during an afternoon, a condition favorable for the operation of a precision balance. Adjacent to the balance room was a small observation room from which the balance could be operated without entering the balance room. The rooms were constructed with a minimum of magnetic material so placed that all magnetic masses of appreciable size were at a considerable distance from the balance. Inside the balance room were nonmagnetic piers each having a heavy top of statuary marble.

1. THE BALANCE

A 2-kilogram precision balance with a 30-cm beam was used, the same one as was employed in the work of 1911, when all the magnetic parts except the knife edges were removed. In the course of the present investigation, the knife edges were reground and heavy agate planes substituted for those originally furnished. As shown in figures 1 and 2, the balance was mounted on three marble blocks attached to the marble top of the coil case. On top of the blocks was a hole-slot-plane system arranged to hold the three supporting feet of the balance case. Slides were attached to the pieces holding the hole and the slot so that the balance with the attached moving coil could be moved in two horizontal directions, thus providing the horizontal adjustments of the moving coil with respect to the fixed coils. The moving coil was suspended from the right-hand pan of the balance by means of a tube through which the leads to the moving coil were carried.

A device was installed by which a cylindrical weight could be added to, or removed from, the pan without arresting the balance. The device had, projecting over the pan, an arm with 3 ivory fingers which could be moved between 4 ivory fingers attached to the pan. Grooves in both sets of fingers prevented a cylindrical weight from rolling out of place. A cam operated from a distance raised and low-

ered the arm carrying the three ivory fingers, thereby either removing the weight from the balance pan or replacing it. As the weights were placed on the pan to which the moving coil was attached, neither the ratio of the balance arms nor the bending of the beam affected the results.

(a) OPTICAL SYSTEM

The optical system for determining the position of the balance beam consisted of a lamp and scale with a mirror on the balance beam. There were three distinctive features of this system: (1) The light beam was symmetrical with respect to the 2 arms of the balance beam so that any heating produced by the light affected the 2 arms equally; (2) the effective length of the optical lever was doubled by an arrangement of mirrors which gave 2 reflections of the light from the mirror on the balance beam, thus doubling the motion of the spot of light on the scale so that this motion was then about 72 times the motion of the moving coil; (3) right-angled prisms with optical surfaces were used for most of the reflectors, thus giving a very distinct image on the reading scale. By employing these features the optical system using a lamp and scale was sufficiently accurate and easily operated.

(b) SENSITIVITY OF THE BALANCE

The sensitivity of the balance, with a half period of about 19 seconds, was usually about 3 milliradians per milligram. With the optical system described above, 1 mg placed on the pan produced a deflection of 16 mm on the scale. It was possible to make a weighing to about 0.01 mg since the position of the spot of light on the scale could be read to 0.2 mm. As the total load on the pan was more than 1 kg, a weighing to 0.01 mg required a sensitivity of 1 part in 100 million of the total load on the pan. This sensitivity was necessary to obtain a precision of one part in a million in the electromagnetic force between the coils, since this force seldom exceeded 10 grams.

In addition to the precautions normally taken in precision weighings, the following requirements were essential for the extreme precision needed in this investigation: (1) The balance must not be arrested during a weighing; (2) the temperature of the balance beam must be kept very constant; and (3) the density of the weights on the two pans must be approximately the same. An arrestment of the balance usually changed the rest point, the amount of change being different for each arrestment. A method of weighing will be described later which avoided this difficulty. The balance beam was made of a material which had an expansivity of nearly 20 parts in a million per degree centigrade. A change in temperature of 0.0005° C of one arm relative to the other affected a weighing by a part in 100 million. The method of weighing employed in this investigation eliminated the effect of any slow, uniform drift of temperature. The density of the counterweights was such that the volume occupied by them was about the same as the volume of the coil, so that changes in barometric pressure did not appreciably affect the rest point of the balance during a weighing.

In addition to the difficulties that are inherent in any weighing of extreme precision, the current balance has the added difficulty that the current heats the moving coil, thus causing, in the surrounding air, convection currents which produce a force on the coil. In a

closed space which has reached temperature equilibrium, these convection currents become very stable so that the force is very constant. Hence weighings were made only after the balance and its surroundings had been under constant temperature conditions for several hours. The convection currents, when a moving coil was dissipating 2 watts, produced a force on it of as much as 0.2 mg, but, so long as this force remained constant, it caused no error in the determination of the electromagnetic force which was always obtained by reversing the current in the fixed coils.

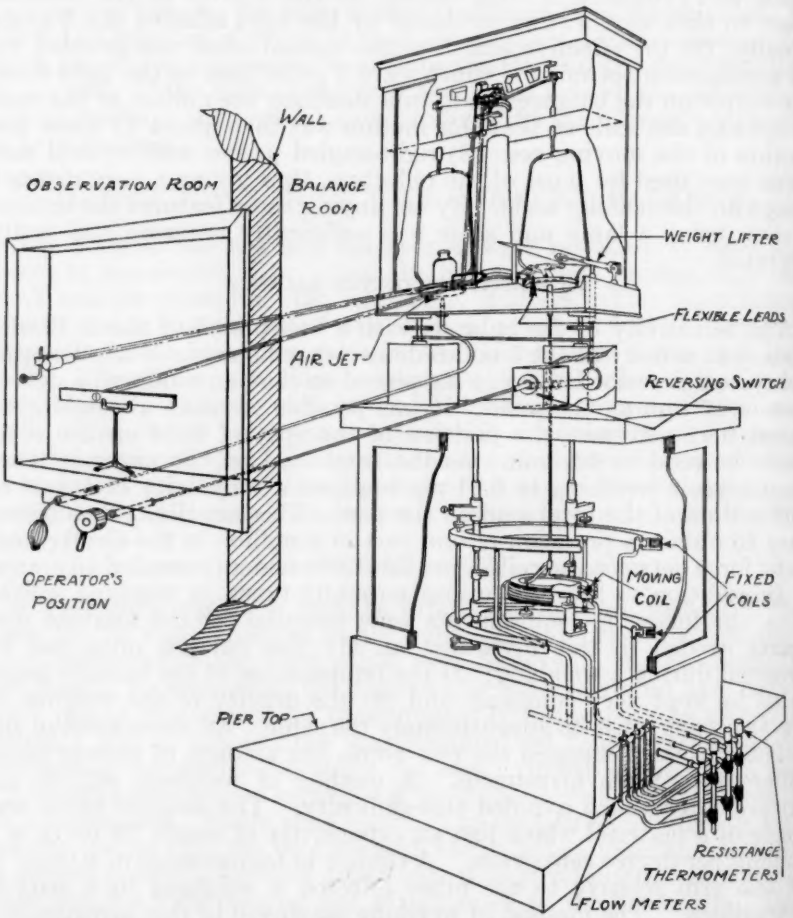

FIGURE 1.—*Assembled current balance and the operator's position.*

(c) THE WEIGHTS

For each combination of coils, 3 special weights were prepared, corresponding to 3 different currents. All these weights were in the form of cylinders with rounded ends. The lengths varied from 2.5 to 3.5 cm. Some were of a gold-platinum alloy, others of a platinum-iridium alloy. They have been frequently calibrated by the mass section of this Bureau and no significant changes in mass have

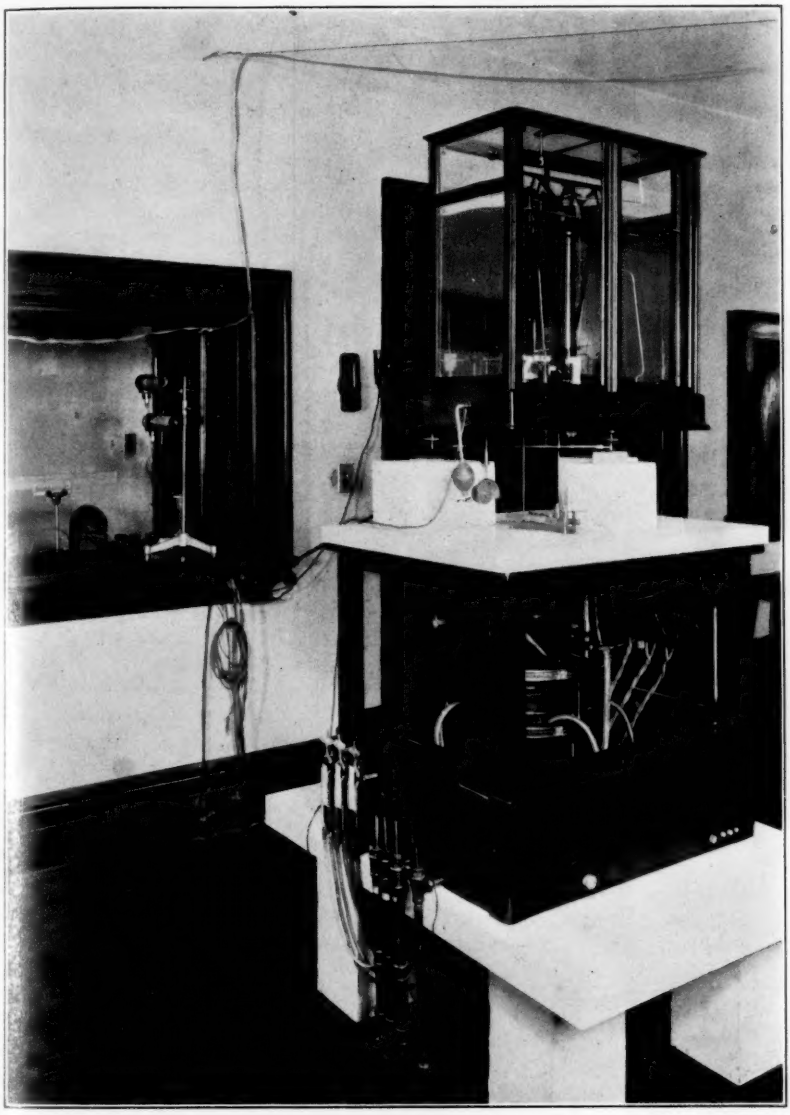

FIGURE 2.—*Photograph of the current balance as used in the final observations, showing the operator's position in an adjoining room.*

The window between the two rooms was closed when observations were being made. Every part of the entire assembly, including the rubber hose for making the water connections, the brass water pipes, and the resistance thermometers in the pipes, was carefully tested and found to be nonmagnetic. The only exceptions were the three steel knife edges of the balance, which were more than a meter from the coils.

UNIV OF MICH.

been observed. The nominal values of the weights are given in table 2, p. 677.

(d) PROCEDURE IN MAKING A WEIGHING

For several hours before the actual weighings started, a current of approximately the same value as that to be used later was sent through the coils. When conditions had become stable the balance beam was released. With the direction of the current such that the electromagnetic force was downward and with the weight off the pan, the counterweight on the opposite pan was adjusted to give a suitable value of the rest point. These adjustments were necessarily made with the operator in the balance room. The operator then went to the observation room and after a short interval (about 15 minutes) began a set of observations. By means of air jets that could be directed under the pan, the amplitude of swing was adjusted to a convenient value, usually about 2 centimeters on the scale. The position of the rest point was then determined by observing 3 turning points at the right and 2 at the left. The direction of the electromagnetic force was then reversed by reversing the current through the fixed coils, and at the same time the weight was placed on the coil pan of the balance so that the total force acting on the balance beam was only slightly changed. A second rest point was then observed in order to obtain the difference in the rest points with the weight on the pan and with it off. As a check, the current in the fixed coils was again reversed and the weight removed. If conditions had remained exactly the same, this third rest point would exactly agree with the first. This was seldom the case, because conditions changed almost continuously. Hence, six or more rest points were usually necessary in order to determine, by a graphical method, the difference in the rest points with the weight on and with it off. From this difference and the sensitivity of the balance, the difference between the gravitational force on the weight and twice the electromagnetic force between the coils could be obtained.

2. COILS AND THEIR MOUNTINGS

The coils were mounted in a case with sides of wood and glass, the bottom of the case being the marble top of a pier, and the top being a marble slab upon which the balance was supported and to the underside of which the fixed coils were attached. The tube by which the moving coil was suspended from the pan of the balance passed through a hole in the marble slab.

(a) THE COILS

Rosa, Dorsey, and Miller constructed 4 moving coils designated as M1, M2, M3, and M4, and 3 pairs of fixed coils designated as S1, S2; L1, L2; and L3, L4. They stated that moving coils M2 and M3 were somewhat superior to M1 and M4 and that L1, L2 were somewhat inferior to either L3, L4 or S1, S2. Hence, for this investigation the moving coils M2 and M3 and the 2 pairs of fixed coils S1, S2, and L3, L4 have been used. The important constants of these coils as determined at the time of winding are given in table 1.

TABLE 1.—*Constants of coils*

[All measured constants were determined at time of winding]

Kind of coil	Designation	Number of windings	Number of turns per layer in each winding	Number of layers	Total number of turns in each winding	Mean radius of coil	Diameter of wire over insulation	Radial depth of winding	Axial width of winding channel	Computed width of winding [a]	Measured width less computed width [b]
						cm	*cm*	*cm*	*cm*	*cm*	*cm*
Moving	M2	2	6	12	72	12.499	0.076$_8$	0.954$_8$	0.956$_4$	0.921$_6$	0.034$_8$
Do	M3	2	7	14	98	10.030	.070$_1$	1.029$_4$	.996$_7$	.981$_4$	.015$_3$
Fixed	S1	2	14	28	392	19.97	.054$_6$	1.528	1.580	1.529	.051
Do	S2	2	14	28	392	19.96	.054$_6$	1.522	1.579	1.529	.050
Do	L3	2	17.972	36	647	25.00	.051$_0$	1.943	1.969	1.833	.136
Do	L4	2	17.972	36	647	25.00	.053$_8$	1.925	1.965	1.927	.038

[a] The computed width of the winding is the product of the total number of turns per layer and the diameter of the wire over the insulation.

[b] In all computations of the force the axial width of the coil was assumed to be equal to the width of the winding channel.

All coils were of enamel-insulated wire wound bifilarly on brass forms. A channel having approximately the dimensions desired for the finished coil was turned in each coil form. The bottom and sides of the channel were insulated with a thin layer of paper. Two wires entered the bottom of the channel from axial holes which were at opposite ends of a diameter. The correct number of turns for the bottom layer was wound, then each wire was brought up to the next layer at a predetermined point. In most coils this point was on the radius at which the winding started. However, in coils L3 and L4 this was not the case, but in each layer the wire was brought up for the next layer at a point 10° (one thirty-sixth of a turn) before reaching the radius at which the layer started. In every coil there was the same number of turns in each of the two windings. The end of each winding was brought out through an axial hole in the form on the same radius as the beginning of the winding. Terminal blocks were so mounted that the external leads could be held in a definite position and could be soldered to the leads from the coil. The form of a terminal block is shown in figure 3.

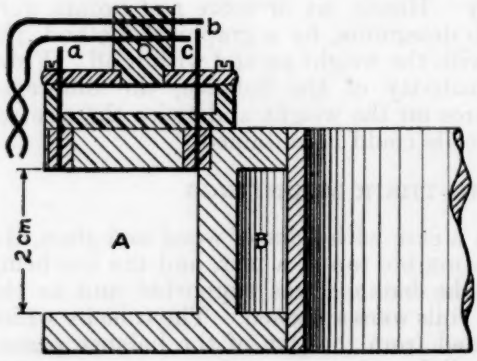

FIGURE 3.—*Crosssection of the form of a large fixed coil at a terminal block, showing the leads.*

The channel in which the wires were wound is A; the water channel is B. The electrical connections between the leads from the winding and the external leads were made by drops of solder: at a and b for normal operation; at b and c for measuring the effect of the leads.

In winding the coils, one or more strips of "onionskin" paper about 0.05 mm thick were placed between layers. In order to prevent moisture from penetrating the coil, the winding was carefully sealed by the following method: ". . . the paper covering the outer layer

of wire was saturated with paraffin melted in with a clean hot soldering copper, the paraffin being well melted to the sides of the form. Then a strip of muslin, well soaked in a hot mixture of beeswax and Venice turpentine, was wrapped around the coil and melted to the underlying paraffin; over the whole was wrapped a strip of binder's cloth soaked in hot paraffin and melted to the muslin and form."[12] The sealing of the coils has not been disturbed since 1910. In this investigation there has been no indication of any imperfection in this sealing.

(b) COIL MOUNTING

As shown in figures 1 and 2, the fixed coils were supported from the marble top of the coil case, and the moving coil was suspended from a pan of the balance. The two fixed coils were maintained parallel and approximately coaxial by three *spacing* rods, and were attached to the marble top by *supporting* rods. A separate set of spacing rods of uniform length was required for each coil combination, the length being such that the electromagnetic force of each fixed coil on the moving coil is a maximum when the moving coil is midway between the fixed coils. The supporting rods permitted the leveling of these coils. The suspension of the moving coil was a tube, the upper end of which was attached to a pan of the balance and the lower end of which carried a tripod. The moving coil was attached to the feet of the tripod by adjusting screws which permitted the coil to be leveled.

(c) COOLING SYSTEM

A cooling system in which water was circulated in a closed circuit was arranged to carry off the heat that was produced by the current in the coils. The water, returning warm from the current balance, flowed through a cooling coil to lower its temperature, then into a tank in which the water was thoroughly stirred and carefully thermostated, the regulation being to about 0.02° C. The water was then pumped by a centrifugal pump to a distributing point inside the coil case. At the distributing point there was a connection to each of the fixed coils and to the water jacket of the moving coil, each of which had a separate return to a junction point from which the water was returned to the cooling coil. In the return circuit of each coil was a valve for regulating the flow, a flowmeter for measuring the flow, and the coil of a resistance thermometer for measuring the temperature of the water. The temperature of the water when it reached the distributing point was measured by a fourth resistance thermometer.

The cooling water for each fixed coil was circulated through a channel in the form on which the coil was wound, as shown in figure 3. The water entered the channel at one end of a diameter and left at the opposite end so that the circulation was in opposite directions in the two halves of the circumference. As a result, the temperature distribution in the form was not exactly uniform. As an example, with 1 ampere in the large fixed coils, the temperature of the outflowing water was 0.5° C. higher than the inflowing. The nonuniformity in temperature caused a slight distortion of the coil which, if appreciable, would cause the results with different currents to be different. In no case was any distortion indicated.

[12] See p. 286 in reference of footnote 8.

Two different types of water jackets have been used for cooling the moving coil, and in addition weighings have been made without any water jacket. The first water jacket consisted of a double-walled copper cylinder having a metal top and bottom with the water circulating in the space between the two walls. In this water jacket, cooling was effected in part by radiation and in part by convection currents which were set up in the air inside the jacket. These convection currents were not always sufficiently steady to permit the most accurate weighing. The second type of water jacket, shown in figure 4, consisted of a channel in a solid piece of brass to which was soldered a spiral copper tube, in which water was circulated. With the coil in this channel, the balance was very steady although the temperature of the coil was somewhat higher than when used in the open air or in the cylindrical water jacket. The type of water jacket

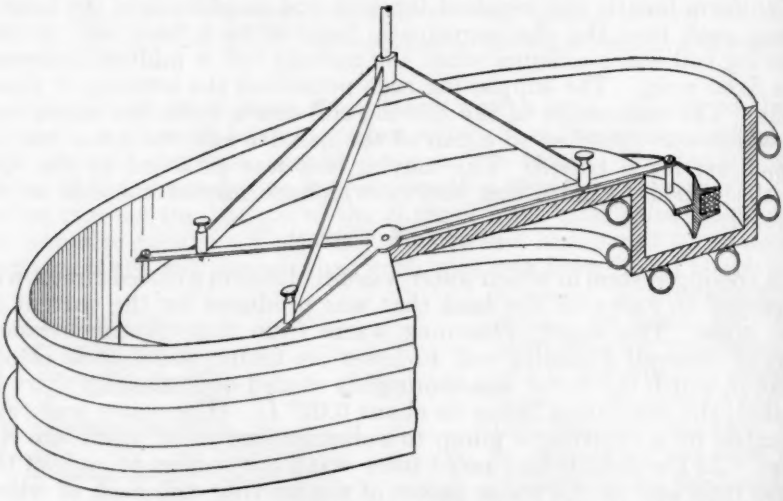

FIGURE 4.—*The second type of water jacket, consisting of a channel in a piece of brass.*

A section is removed to show the moving coil and its mounting. The coil was placed near the bottom of the channel, so that air currents were minimized. The water jacket was cooled by water flowing in the copper tube that was attached to the outside of the channel. The transfer of heat from the brass to the copper tube was facilitated by soldering the tube to the brass.

produced no effect on the result, but the balance was somewhat steadier when the second type was used.

III. ELECTRICAL CIRCUIT OF THE CURRENT BALANCE

The electrical circuit of the current balance was arranged to meet the following conditions: (1) The operator should be able to maintain a constant current; (2) the operator should be able to measure the current in B.S. international amperes by direct comparison with a standard of resistance and a standard cell; (3) the operator should be able to remove a weight from the pan of the balance at a time so nearly simultaneous with the reversal of the current in the fixed coils that the swinging of the balance would not be greatly disturbed; (4) the leads connecting the moving coil to the rest of the circuit

should be of such a character as not to affect materially the sensitivity or reliability of the balance; (5) those parts of the circuit in which thermoelectromotive forces would affect the result should be so designed that these forces would be a minimum; (6) the insulation resistance between the balance coils and ground should be so high that the effect of leakage currents would be negligible; (7) the frame of the moving coil should be at the same potential as the surrounding water jacket so that electrostatic forces in the balance would be eliminated; (8) the leads should be arranged to have as small a magnetic field as possible. These conditions were met with as simple a circuit as could be devised. A diagram of the circuit is shown in figure 5.

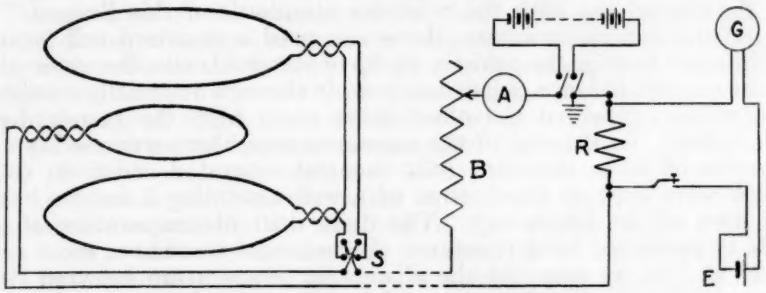

FIGURE 5.—*Electrical circuit of the current balance.*

The current in the current balance coils and the resistance standard, R, was adjusted by the rheostat, B, until the fall in potential across R was exactly equal to the electromotive force of the standard cell, E, as shown by the zero deflection of the galvanometer, G. In this manner the current was measured directly in B.S. international amperes by the ratio of E to R. The ammeter, A, was used for obtaining a rough adjustment of the current. The circular reversing switch, S, reversed the current through the fixed coils only, thus reversing the electromagnetic force on the moving coil.

1. CONSTANCY OF CURRENT

The constancy of the current depended largely on the storage battery which was used as a source, but was influenced to some extent by the temperature conditions in the copper portions of the circuit. The battery which gave most satisfactory constancy was a 100-volt, 400-ampere-hour lead storage battery. The current changed so slowly that the operator could maintain it constant to a part in a million by adjusting a resistor once or twice a minute.

2. MEASUREMENT OF THE CURRENT IN B.S. INTERNATIONAL AMPERES

The current was measured in B.S. international amperes by comparing the potential drop produced by it in a standard resistance with the electromotive force of a standard cell. As shown in figure 5 a standard cell, E, in series with a key and sensitive galvanometer, was connected directly to the potential terminals of a four-terminal resistance standard, R. The current was then adjusted by the rheostat, B, until the deflection of the galvanometer was zero. For this condition the current, I, in B.S. amperes was equal to E/R, where E is the B.S. value for the electromotive force of that particular standard cell, and R is the B.S. value of the resistance of that particular standard resistor.

The standard resistors used in this set-up were specially designed to carry a large current without change in resistance. They were

made of manganin strip 5 millimeters wide, and thick enough to give the desired resistance in a length of about 5 meters. This strip was wound between a series of insulated posts and the whole immersed in oil maintained at a constant temperature. The temperature coefficient of resistance was usually about 5×10^{-6} per degree centigrade and the load coefficient about 1×10^{-6} per watt. In order that the current could be determined to a part in a million, the temperature had to be measured to 0.2° C and the power to 1 watt. These resistors were frequently measured by the resistance section of this Bureau. Their value at any particular time was known to one or two parts in a million.

The standard cell employed at any particular time was compared on the day of use with the reference standards of this Bureau. In many of the measurements, there was used a standard cell located in the same bath as the primary group of standard cells, the connection to the current-balance circuit being made through a specially insulated line which connected the observation room with the standard-cell laboratory. In the rest of the measurements, there was used one of a group of three standard cells (neutral saturated cadmium cells) which were kept at the bottom of a well extending 3 meters below the floor of the laboratory. The daily drift of temperature of the cells as measured by a resistance thermometer was never more than 0.02° C. In no case did the change in temperature between time of use and time of comparison with the standard group amount to as much as 0.01° C, which would change the electromotive force of the cell less than ½ microvolt.

The cell employed in any set of observations was connected almost continuously for several hours. Small currents, seldom more than 0.01 microampere, passed through the cell, sometimes in the positive, sometimes in the negative direction. No change in the electromotive force of the cell due to this cause was ever detected.

The sensitivity of the galvanometer was 0.8 radians per microampere and its external critical damping resistance was 500 ohms. At a scale distance of 6.2 meters a current of 2×10^{-9} ampere produced 1 centimeter scale deflection. Since the resistance of the galvanometer was about 42 ohms and that of the standard cell about 500 ohms, an unbalanced electromotive force in the galvanometer circuit of 1 microvolt, corresponding to a change in the current through the current balance of a part in a million, produced a deflection of nearly 1 centimeter. The galvanometer had ample sensitivity and, as normally used, was critically damped.

A disadvantage of the method just described for measuring the current in B.S. amperes was its lack of flexibility. For a given resistance and standard cell, a definite current was required. With this current and a given set of coils in the current balance, the weight necessary to counterbalance the electromagnetic force was fixed. Hence a weight had to be constructed for each resistance that was used in conjunction with each set of coils. Twelve weights were made, the nominal values of which are given in table 2. Extremely precise adjustment of the weights is not necessary since differences in force as large as 1 milligram could be obtained from changes in the rest point of the balance.

TABLE 2.—*Nominal masses of weights used with different resistances and different coil combinations*

Coil combination	Composition	Density	R=1 ohm I=1.018 amp	R=1.5 ohm I=0.679 amp	R=2.0 ohm I=0.509 amp
	Percent	*g/cc*	*grams*	*grams*	*grams*
S1 S2 M3	90 Au 10 Pt	19.5	8.81	3.91	2.20
L3 L4 M2	90 Au 10 Pt	19.5	10.55	4.68	2.64
S1 S2 M2	90 Pt 10 Ir	21.5	11.92	5.29	2.96
L3 L4 M3	90 Au 10 Pt	19.5	8.43	3.75	2.09

3. REVERSAL OF CURRENT IN THE FIXED COILS

The reversal of the current in the fixed coils presented both an electrical and a mechanical problem. The reversal should not produce such high induced electromotive forces as to endanger the insulation of the coils, and the effective time of reversal should so nearly coincide with the time at which the weight is added or removed that no large change would be produced in the amplitude of swing of the balance. Both of these problems were solved by the use of a step-by-step reversing switch which was mounted on the same shaft as a cam which controlled the addition or removal of the weight. The reversing switch [13] was of the rotary type so designed that a rotation of about 160° first decreased the current in five steps to about one tenth its original value, reversed this small current, then increased it to its original value in five steps. The complete operation of the switch could be accomplished in a fraction of a second. The cam of the weight lifter was so oriented on the shaft of the reversing switch that the weight would be added or removed at the proper time. An operator learned from experience the position in the swing of the balance at which a certain speed of rotation of the shaft produced a minimum disturbance of the balance. The reversal did not ordinarily change the amplitude of swing by more than a few centimeters on the scale. The amplitude of swing could be adjusted from the observation room by means of air jets under the pans. Any lateral swinging of the pans could be observed by an auxiliary optical system and could be damped by lightly pressing against the pan a camel's-hair brush which could be operated from the observation room.

4. LEADS TO THE MOVING COIL

The moving coil was connected to the electrical circuit at terminals in the balance case from which flexible leads extended to terminals on the pan of the balance. Rigid leads, passing through the tube that supported the moving coil, connected the terminals on the pan to wires that were connected to the windings of the coil. The sensitivity of the balance was not affected by the rigid leads, but was affected by the flexible leads. The flexible leads were made as pliable as possible in order that they would produce a minimum effect on the sensitivity of the balance, and were so arranged that air currents produced by the heating of them did not appreciably disturb the balance. They consisted of two sets of fine copper wires, each set extending from a terminal in a terminal block mounted on the balance

[13] See p. 295 in reference of footnote 8.

pan to a terminal in an identical block on the balance case. Each terminal block consisted of two strips which were cut from a threaded brass tube and which were insulated by being attached to opposite sides of two short amber cylinders. About 36 copper wires each 0.025 mm in diameter extended from each strip of one block to the corresponding strip of the other block. The strips on the pan were connected to the rigid leads of the moving coil, while the strips in the balance case were connected to the main circuit. A sketch of the leads showing their relation to the weight lifter and balance pan is given in figure 6.

In order to construct a set of leads, the terminal blocks were removed from the balance and mounted in a frame which held them 8 centimeters apart. The fine copper wire was wound around the two cylinders, the spacing between wires being 1 or 2 millimeters. The wires were soldered to the strips, then the portions of wire between the two strips of each block were removed. The two sets were then mounted in the balance with the strips horizontal and the wires were annealed by heating to a dull red by passing a current through them. During the annealing process, a small glass rod was placed on each of the two sets of wires, the upper and the lower, so as to obtain uniformity in the shape of the system of wires. The two sets when connected in series had a resistance of about 0.13 ohm. The heat generated in these wires by the current was sufficient to cause, in the air, appreciable convection currents which were deflected away from the balance beam by a shield placed directly above the wires. However, there was a buoyant effect on the leads themselves which, with a current of 1 ampere, produced a force on the pan of the balance of 0.15 mg. This force was very constant, thus introducing no difficulty in making a weighing and producing no error in the result since it was independent of the direction of the current.

In addition to the current leads just described, there were two potential leads connected to the terminals of the winding of the moving coil, and one grounding lead connected to its frame. The portion of each of these leads which extended from the balance case to the pan consisted of a single fine wire. The potential leads were used in measuring the resistance of the moving coil. The grounding lead was used to connect the frame of the coil to earth.

The flexible leads appreciably affected the sensitivity of the balance. In one case a sensitivity of 2.2 cm/mg was reduced to 1.2 cm/mg by installing a set of leads. However, sufficient sensitivity could always be obtained by adjusting the center of gravity of the moving system of the balance.

5. THERMAL ELECTROMOTIVE FORCES

The only part of the circuit in which a thermal electromotive force would influence the result was the closed loop which included the standard cell, galvanometer, and standard of resistance. All parts of this loop were of copper except the standard resistor and standard cell, both of which were kept at a constant temperature. The conducting parts of the galvanometer were entirely of copper, and all keys, switches, and binding posts were made of copper. Two different tests were used to determine the thermal electromotive force in this loop. In the first test, a series of observations was made in which

55945—34—2

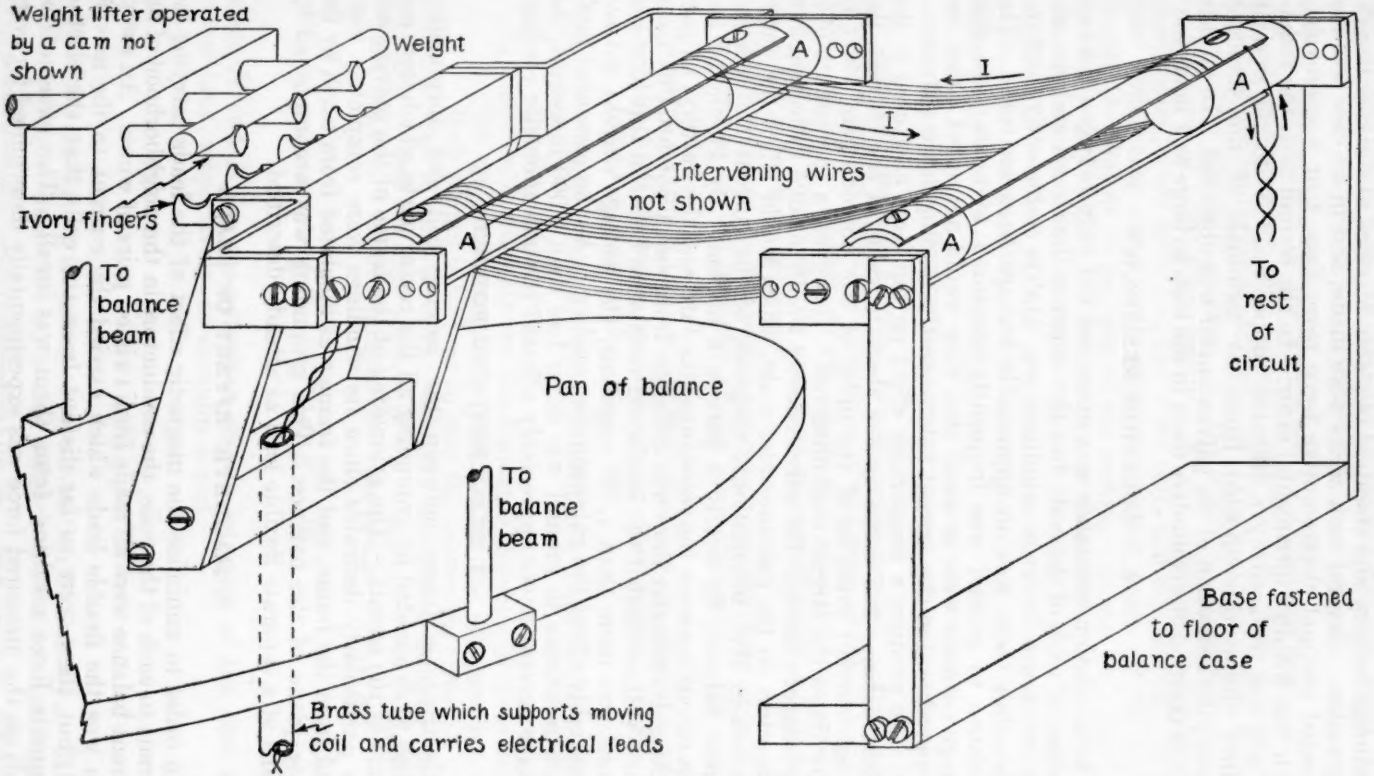

FIGURE 6.—*The flexible leads and the weight lifter, showing their relation to the pan of the balance.*

The amber cylinders, marked A, served to separate and insulate the brass strips to which the fine, flexible wires were attached. The potential and grounding leads are not shown.

the storage battery and standard cell were reversed at the end of each observation. Several such series were made, and in no case was the indicated thermal electromotive force more than 2 or 3 microvolts, which was within experimental error. In the second test, the standard cell was replaced by a 500-ohm copper coil. With the current balance circuit disconnected from the terminals of the standard resistor, the deflection of the galvanometer was observed. In no case was the thermal electromotive force in the loop as large as 1 microvolt.

6. INSULATION RESISTANCE

The insulation resistance was measured not only between the two windings of each of the coils, but also between the circuit and ground. The resistance between windings was always sufficiently high to insure that there was no appreciable leakage between turns. The resistance to ground was frequently measured to make sure that leakage currents were so small that they would not affect either the force produced in the current balance or the reading of the galvanometer. To produce a measurable effect on the force measured in the current balance and hence on the absolute value of the current, the leakage current must be of the order of one microampere which is many times the largest ever observed. However, a thousandth of a microampere through the galvanometer would make a deflection of 5 millimeters on the galvanometer scale, which would affect the measurement in B.S. international amperes, of the current through the current balance, by nearly a part in a million. By grounding the main circuit between the resistance standard and the battery, no part of the galvanometer loop was different from earth potential by more than 1 volt, so that if the insulation resistance between this loop and ground was more than 1,000 megohms, the leakage current did not appreciably affect the galvanometer reading. As the measured insulation resistance to ground was never less than 6,000 megohms, the leakage current never appreciably affected the galvanometer reading.

7. ELECTROSTATIC FORCES

Electrostatic forces between the moving coil and surrounding bodies were avoided by grounding all the metal parts which were not a part of the circuit. The grounding of the frame of the moving coil was particularly desirable since its windings were completely insulated from the frame, and the frame was insulated from earth by the agate plane of the balance. This grounding was accomplished by means of a separate flexible lead as already described.

8. MAGNETIC EFFECT OF LEADS

In order to minimize the magnetic effect of the leads carrying the current to each of the coils, the conductors in the neighborhood of the current balance were all made from twisted pairs of wires. An exception was the flexible leads which carried the current to the moving coil, but these were so far distant from the coils that the electromagnetic force resulting from them was small. The effect of the leads on the measured force was experimentally determined for every set-up by a method described later.

IV. COMPUTATION OF THE MAXIMUM FORCE FOR UNIT CURRENT

The computation of the maximum force between the coils of a current balance when unit current flows through each of them may be considered under three headings: (1) The maximum force between two circular coaxial filaments; (2) the maximum force between two coaxial coils of finite cross section; (3) the maximum force between three maladjusted coils; i.e., two fixed coils and one moving coil, the fixed coils being not exactly coaxial and not quite at the correct spacing, so that at no position of the moving coil can both exert the maximum force on it. The first two of these were computed from observed data taken on the coils before mounting them in the current balance. The effect of lack of coaxiality and of variation from the position for maximum force was determined from experimental data taken in the course of weighings.

1. MAXIMUM FORCE BETWEEN CIRCULAR FILAMENTS

The maximum force between two filaments located at the circumference of coaxial circles is a function of the ratio of the radii of the circles and of the currents in the filaments. This force for unit current in each filament can be expressed in mathematical notation by use of the following symbols: [14]

Let a_1 = radius of the filament at the circumference of the larger circle

a_2 = radius of the filament at the circumference of the smaller circle.

$\alpha = a_2/a_1$ = ratio of radii of the filaments (always less than unity)

z_m = the axial distance between the circular filaments when the force is a maximum

$y_m = \frac{z_m}{a_1}$ = ratio of axial distance for maximum force to the radius of the larger filament

F_m = force in dynes between the filaments carrying unit current in the cgs electromagnetic system when the distance between their planes is such as to give the maximum force.

The units used in measuring the radii are immaterial so long as the same unit is used for both since only the ratio enters the formula.

Then Maxwell's elliptic-integral formula can be written as

$$F_m = \frac{\pi y_m k}{\sqrt{\alpha}}\left\{\frac{2-k^2}{1-k^2}E - 2K\right\} \tag{1}$$

where K and E are the complete elliptic integrals of the first and second kind, respectively, to modulus k and

$$k^2 = \frac{4\alpha}{(1+\alpha)^2 + y_m^2} \tag{2}$$

The formula for F_m is expressed as a function of α and y_m. However, it can be shown that y_m is also a function of α so that F_m is a

[14] The nomenclature used in this paper corresponds with that used by Snow (footnote 25). This is somewhat different from that used by Rosa, Dorsey, and Miller (footnote 8), and by Grover (footnote 15).

function of α only. No formula for computing F_m has been developed which does not first require the computing of y_m. An exact formula for computing y_m as a function of α has been given by Grover [15] who also gives a table of y_m as a function of α. The following empirical formula derived from Grover's table gives y_m with an accuracy of at least a part in a thousand in the indicated range of α, which accuracy is sufficient for computing F_m to a part in a million. The formula is

$$y_m = 0.5 - \frac{9}{20}\alpha^2 - \frac{1}{16}\alpha^4 \quad 0 < \alpha < 0.75 \tag{3}$$

It has been shown [16] that a variation in y_m produces a variation in F_m which is given by the equation

$$\frac{\Delta F_m}{F_m} = -c\left(\frac{\Delta y_m}{y_m}\right)^2 \tag{4}$$

where c varies between 0.6 and 0.7 for the values of α used in this investigation. This equation substantiates the statement of the required accuracy in y_m that was made in the previous paragraph. While y_m does not need to be accurately known, the value of α is required with great precision. This can be seen from the formula [17]

$$\frac{\Delta F_m}{F_m} = \epsilon\frac{\Delta\alpha}{\alpha} \tag{5}$$

where ϵ varies between 2.0 and 4.2 in the range of α considered. Actual values of ϵ for the coils used are given in table 11.

The values of the elliptic integrals necessary for computing F_m are given in various tables, but only in Legendre's [18] with sufficient accuracy, since the difference of two quantities having about the same value is required. The interpolation in Legendre's tables is exceedingly laborious. Rosa, Dorsey, and Miller [19] used these tables for computing their table XXX from which F_m can be determined, but the range of the table is not sufficient to cover one combination of coils used in this investigation. Grover [20] has given, for the entire range of α, tables which are easy to use and by which all values of F_m in this paper have been computed. However, all values have been checked by a method based on the use of arithmetico-geometric means [21] for computing the elliptic integrals. This method so simplifies the computation of F_m that the use of auxiliary tables is unnecessary.

The first step of the computation is to form a table of arithmetico-geometric means defined as follows: (Note that the a's in this table are not the radii of the coils).

[15] B.S. Bull., vol. 12, p. 317, 1915.
[16] Equation 64 on p. 344 of Grover's paper. Reference, footnote 15.
[17] The ϵ in the formula is the same as the ϵ given on p. 330 of the paper describing the work in 1911. Reference, footnote 8.
[18] A photographic reproduction of the original tables was published by K. Wittwer, Stuttgart, in 1931.
[19] Reference footnote 8.
[20] Reference footnote 15.
[21] For a complete discussion of the method see King, On the Direct Numerical Calculation of Elliptic Functions and Integrals. Cambridge Univ. Press, 1924. See also Grover, Phil. Mag., series 7, vol. 15, p. 1115, 1933.

$a_0=1$	$b_0=\sqrt{1-k^2}$	$c_0=k$
$a_1=\frac{1}{2}(a_0+b_0)$	$b_1=\sqrt{a_0b_0}$	$c_1=\frac{1}{2}(a_0-b_0)$
$a_2=\frac{1}{2}(a_1+b_1)$	$b_2=\sqrt{a_1b_1}$	$c_2=\frac{1}{2}(a_1-b_1)$
$a_3=\frac{1}{2}(a_2+b_2)$	$b_3=\sqrt{a_2b_2}$	$c_3=\frac{1}{2}(a_2-b_2)$
.	.	.
.	.	.
.	.	.
a_n	b_n	c_n

The values of a_n rapidly approach those of b_n, so that c_n approaches zero. When $\alpha=0.75$, a_4 differs from b_4 by less than a part in 10 million; for smaller values of α, the difference is less. In most cases the table does not need to be computed beyond a_3. Then by substituting, in equation 1, the values of the elliptic integrals, K and E, as given by the arithmetico-geometric means,

$$F_m=\frac{\pi^2 y_m k}{4a_n(1-k^2)\sqrt{\alpha}}\{k^4-2(2-k^2)(c_1^2+2c_2^2+4c_3^2+\cdot\cdot\cdot\cdot\cdot)\} \quad (6)$$

The following example in which the value of α is the largest of any used, illustrates the method of computation.

Example: Computation for coils S1 M2

$$\alpha=0.6258941$$

By formula 3, four significant figures of the value of y_m can be obtained, so that for the computation

$$y_m=0.3141000$$

By formula 2

$$k^2=0.9129842$$

Forming the table of arithmetico-geometrical means

$a_0=1$	$b_0=0.2949845$	$c_0=0.9555021$
$a_1=0.6474922$	$b_1=0.5431247$	$c_1=0.3525078$
$a_2=0.5953085$	$b_2=0.5930169$	$c_2=0.0521837$
$a_3=0.5941627$	$b_3=0.5941616$	$c_3=0.0011458$
$a_4=0.5941621$	$b_4=0.5941621$	$c_4=0.0000006$

Since $a_4=b_4$; $a_4=a_5=\cdot\cdot\cdot\cdot\cdot=a_n$.

Substituting in formula 6

$$\begin{aligned}
c_1^2 &= 0.1242617\\
2c_2^2 &= 0.0054463\\
4c_3^2 &= 0.0000053\\
c_1^2+2c_2^2+4c_3^2 &= 0.1297133\\
2(2-k^2) &= 2.1740316\\
k_4 &= 0.8335401\\
2(2-k^2)(c_1^2+2c_2^2+4c_3^2) &= 0.2820007\\
k^4-2(2-k^2)(c_1^2+2c_2^2+4c_3^2) &= 0.5515394\\
\pi^2 y_m k &= 2.962097\\
4a_n(1-k^2)\sqrt{\alpha} &= 0.1636115\\
\frac{\pi^2 y_m k}{4a_n(1-k^2)\sqrt{\alpha}} &= 18.10446
\end{aligned}$$

$$F_m=18.10446\times 0.5515393$$

$$=9.985322 \text{ dynes for a cgs unit of current in each filament.}$$

The constants entering into the formula do not all have to be computed with the same accuracy. For instance, the value of y_m need be known only with an accuracy of a part in a thousand to give an accuracy of a part in a million in the value of F_m, as shown by formula 4. However, it is important that the value of y_m should be used in the computation as though it were known to a part in a million, since it enters as a factor in the final product. Other factors also depend on y_m so that the effect of small changes in its value will be compensated in the final result. The value of F_m also depends on the factor $(1-k^2)$. But since, in the example, k^2 is more than 0.9, its value must be given to a part in 10,000,000 if $1-k^2$ is to be known to a part in a million. In this case, the last figure in the value of k^2 is unimportant, but the value chosen must be used throughout the computation.

The value of F_m agrees with that obtained by using Nagaoka's formula [22] and also by interpolation in Grover's tables.[23] The value is doubtless correct to at least a part in a million. The value of α used in this computation required an unfavorable interpolation in the tables of Nagaoka and Sakurai [24] so that a slightly different result was obtained by their use.

2. MAXIMUM FORCE BETWEEN COAXIAL COILS

The maximum force, $\mathfrak{F}_m$, between two circular coils having rectangular cross sections and carrying unit current in each turn, is, to a first approximation, equal to the maximum force, F_m, between two filaments carrying unit current and located at the geometric centers of the cross sections of the coils multiplied by the product of the number of turns in one coil and the number in the second. A second approximation can be obtained by adding a function which includes, in addition to the ratio of the radii of the circular filaments, the ratio of each cross-sectional dimension to the radius of its filament. A further refinement takes account of the fact that, for coils of finite cross section, the axial distance for maximum force may not be the same as the corresponding axial distance for the filaments located at the centers of their cross sections. A formula which takes all these factors into account was derived [25] on the assumption that the coils were composed of a number of circular hoops of insulated wire arranged within a rectangle of dimensions 2b and 2c (see fig. 7), all the n hoops being cut by a radial plane in which the current is transferred from hoop to hoop and in which the current enters and leaves the coil. The same current flows in each hoop, and the magnetic field is symmetrical around the axis of the coil. The equation is [26]

$$\mathfrak{F}_m = n_1 n_2 F_m \left\{ 1 + \Delta_2 + \Delta_4 + \frac{(x\Delta'_2)^2}{2\lambda_2} \right\} \tag{7}$$

In this formula the symbols have the following significance:

n_1 and n_2 = number of turns of wire in the larger coil and the smaller coil, respectively.

---

[22] Phil, Mag., vol. 6, p. 19, 1903. Also given in Grover's paper.

[23] See table 4, p. 372, of Grover's paper. Reference footnote 15.

[24] Sci. Papers of Inst. of Phys. and Chem. Research, Tokyo, table no. 2, 1927. Values of $\frac{\sqrt{a_1 a_2}}{z} F$ are tabulated as a function of k^2.

[25] C. Snow, The Attraction Between Coils in the Rayleigh Current Balance, B.S. Jour. Research, vol. 11, p. 681, 1933. This formula was developed as a part of this research.

[26] The subscripts 2 and 4 for the Δ's were chosen because Δ_2 represents the second-order terms in the Taylor expansion, while Δ_4 represents the fourth-order terms. The term in Δ'_2 takes account of the fact that the z_m used with the coils is not the same as the z_m calculated for the filaments.

F_m = the maximum force for unit current in two filaments located at the centers of the cross sections of the coils. (See equation 1 or its equivalent equation 6.)

a_1 and a_2 = the mean radii of the larger coil and the smaller coil, respectively,

b_1 and b_2 = one half the axial width of the larger coil and the smaller coil, respectively,

c_1 and c_2 = one half the radial depth of the larger coil and the smaller coil, respectively,

$$\alpha = a_2/a_1$$

$$A^2 = a_1^2 + a_2^2 \tag{8}$$

$$\beta = \frac{1-\alpha^2}{1+\alpha^2} \tag{9}$$

$$y_m = 0.5 - \frac{9}{20}\alpha^2 - \frac{1}{16}\alpha^4 \quad \text{if } 0 < \alpha < 0.75 \tag{10}$$

$$x = \frac{y_m}{\sqrt{1+\alpha^2}} \tag{11}$$

λ_1 = zero[27]

$$\lambda_2 = \frac{3\beta^2 - 2x^2}{\beta^2 + 2x^2 + x^4} \tag{12}$$

$$\lambda_3 = \frac{4x^2 + \lambda_2(11x^4 + 10x^2 - \beta^2)}{\beta^2 + 2x^2 + x^4} \tag{13}$$

$$\lambda_4 = \frac{16x^2\lambda_3(x^2+1) - 3x^2\lambda_2(23x^2+8)}{\beta^2 + 2x^2 + x^4} \tag{14}$$

$$B_1 = \frac{c_1^2}{a_1^2}[5(b_1^2 + b_2^2 - c_2^2) - 3c_1^2] - \frac{c_2^2}{a_2^2}[5(b_1^2 + b_2^2 - c_1^2) - 3c_2^2] \tag{15}$$

$$B_2 = \frac{c_1^2}{a_1^2}[5(b_1^2 + b_2^2 - c_2^2) - 3c_1^2] + \frac{c_2^2}{a_2^2}[5(b_1^2 + b_2^2 - c_1^2) - 3c_2^2] \tag{16}$$

$$B_3 = \frac{c_1^2}{a_1^2}[9c_1^2 + 15c_2^2 - 10(b_1^2 + b_2^2)] + \frac{c_2^2}{a_2^2}[9c_2^2 + 15c_1^2 - 10(b_1^2 + b_2^2)] \tag{17}$$

$$B_4 = \frac{1}{A^2}[10(b_1^2c_1^2 + b_2^2c_2^2) - 10(b_1^2 - c_1^2)(b_2^2 - c_2^2) - 3(b_1^4 + c_1^4 + b_2^4 + c_2^4)] \tag{18}$$

$$\Delta_2 = \frac{1}{12x^2}\left\{\left[\frac{c_2^2}{a_2^2} - \frac{c_1^2}{a_1^2}\right]\beta + \frac{2[c_1^2 - b_1^2 + c_2^2 - b_2^2]\lambda_2}{A^2}\right\} \tag{19}$$

$$\Delta_4 = \frac{1}{360A^2x^4}\left\{B_4\lambda_4 + (\beta B_1 - x^2B_2)\lambda_3 + \left[3\beta B_1 - x^2B_3 - 5x^4\left(\frac{c_1c_2A}{a_1a_2}\right)^2\right]\lambda_2 - 6\beta B_1\right\} \tag{20}$$

$$x\Delta_2' = \frac{1}{12x^2}\left\{2\beta\left(\frac{c_1^2}{a_1^2} - \frac{c_2^2}{a_2^2}\right) + \left[(x^2-\beta)\frac{c_1^2}{a_1^2} + (x^2+\beta)\frac{c_2^2}{a_2^2}\right]\lambda_2 + \frac{2(b_1^2 - c_1^2 + b_2^2 - c_2^2)}{A^2}\lambda_3\right\} \tag{21}$$

[27] In the general equation for the force at any distance as developed by Snow, the coefficient λ_1 appears. For the position of maximum force which is considered in this paper, λ_1 equals zero, and the expressions for λ_2, λ_3, and λ_4 are simplified.

The values of F_m, Δ_2, Δ_4, and $\mathfrak{F}_m$ for each pair of fixed and moving coils used in this investigation are given in table 13, p. 727.

3. MAXIMUM FORCE FOR THREE MALADJUSTED COILS

In a current balance of 3 coils, the 2 fixed coils held rigidly together, it is impractical to adjust the coils so that each fixed coil is placed in the exact position relative to the moving coil which was assumed in deriving the formula for the maximum force ($\mathfrak{F}_m$ of equation 7). Some of the adjustments can be made with sufficient accuracy, but for others, corrections must be made to the maximum force to allow for the maladjustment. Hence a discussion of the effect on the maximum force of all the possible maladjustments of each of the coils will be given, together with methods for determining the corrections for these maladjustments.

Each of the three coils used in the current balance can be considered as a solid having 6 degrees of freedom. Any change in position of a coil can be completely described by giving the translations of the center in the direction of three coordinate axes and the rotations relative to the same three axes. However, the rotation of a circular coil around its axis does not influence its magnetic effect because of its symmetry with respect to this axis. Hence, if 1 of the coordinate axes coincides with the axis of the coil, only 5 constants (3 translations and 2 rotations) are required to completely describe any magnetic effect of the coil. For this reason, a coil as used in a current balance is said to have 5 degrees of freedom. It follows that with 3 coils there are 15 independent adjustments but of these the 3 translations of 1 of the coils can be given arbitrary values. Hence, there are only 12 independent adjustments which must be accurately made or for which corrections must be applied to the computed force because of their maladjustment. The adjustments for the two rotations of each coil relative to the horizontal axes were made by levels. The permissible error in each of these two adjustments is $\pm 5'$, a condition which was readily met.

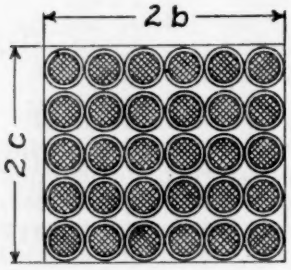

FIGURE 7.—*Method of defining the cross-sectional dimensions of a rectangular coil wound with round insulated wire.*

The axial width is $2b$ and the radial depth is $2c$. In each case, the dimension is the product of the number of wires times the distance between their centers.

With the 6 rotations correctly made, there remain the adjustments for 6 translations, 3 for the moving coil and 3 for one of the fixed coils. If the adjustments were perfect, the centers of the coils would be on the same vertical axis and at such a distance apart that the force between each fixed coil and the moving coil is a maximum. Instead of attempting to make perfect adjustments, it was more convenient, in some cases, to make approximate adjustments and to apply small corrections for any maladjustments that remained. In order to obtain the corrections for these maladjustments, a series of determinations of the force was made with different positions of the moving coil, but with a constant current in the coils. The data were interpreted by a graphical method.

The principle underlying the graphical method can be illustrated by considering the force acting on the moving coil when the three coils are

coaxial and the distance between the fixed coils is so large that when the moving coil is in the midplane neither coil exerts its maximum force. The coil arrangement is shown in figure 8. The two fixed coils, 1 and 2, are so nearly identical, that the value of z_m may be taken as the same for both coils. The force, $\mathfrak{F}$, on the moving coil at a distance z from one of the fixed coils is less than the maximum

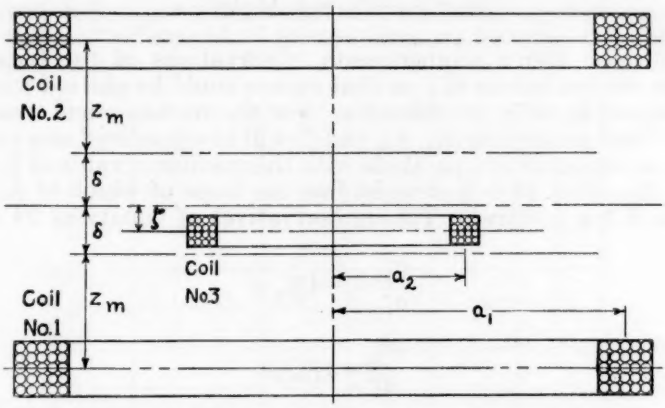

FIGURE 8.—*Nomenclature when the large coils are not correctly spaced.*

force, $\mathfrak{F}_m$, between these coils by an amount which, as a first approximation,[28], depends on the square of the displacement from the position of maximum force. Expressed as equations

$$\mathfrak{F}_{13} = \mathfrak{F}_m[1-\gamma(z_1-z_m)^2] = \mathfrak{F}_m[1-\gamma(\delta-\zeta)^2] \tag{22}$$

$$\mathfrak{F}_{23} = (\mathfrak{F}_m+\epsilon)[1-\gamma(z_2-z_m)^2] = (\mathfrak{F}_m+\epsilon)[1-\gamma(\delta+\zeta)^2] \tag{23}$$

where

$\mathfrak{F}_{13}$ = the downward force between coils 1 and 3 if the distance between them is z_1 and the current is in the same direction in both coils

$\mathfrak{F}_{23}$ = the downward force between coils 2 and 3 if the distance between them is z_2 and the current is in opposite direction in the two coils

$\mathfrak{F}_m$ = the computed maximum force between coils 1 and 3

ϵ = the small amount by which the computed force between coils 2 and 3 is larger than that between 1 and 3

z_m = the distance between a fixed and a moving coil for maximum force

γ = a positive constant, the value of which does not need to be known

δ = the distance from the midplane to the position of the maximum force. The sign of δ is positive if $z_1+z_2>2z_m$

ζ = the displacement of the moving coil below the midplane.

The above equations can readily be derived by Taylor's theorem since, at the maximum, all derivatives except the second are negligible.

The force was not measured for each coil separately, but first for the two fixed coils so connected that the force on the moving coil was the sum of the two forces and then with the current in one fixed

[28] On p. 380 et seq, of the 1911 paper, it is shown that this approximation is sufficiently accurate. A complete discussion is given there of these corrections. Reference footnote 8.

coil reversed (in coil 2 in equation 25), giving the difference of the two forces when the current is in the same direction in all three coils. Then, neglecting the term which is the product of ϵ and another small quantity, the equations of the sum and difference of the forces are:

$$\mathfrak{F}_s = \mathfrak{F}_{13} + \mathfrak{F}_{23} = 2\mathfrak{F}_m[1 - \gamma(\delta^2 + \zeta^2)] + \epsilon \tag{24}$$

$$\mathfrak{F}_d = \mathfrak{F}_{13} - \mathfrak{F}_{23} = \mathfrak{F}_m[4\gamma\delta\zeta] - \epsilon \tag{25}$$

For both the above arrangements, observations of the force were made at several values of ζ so that curves could be plotted with ζ as abscissa and $\mathfrak{F}_s$ or $\mathfrak{F}_d$ as ordinates. For the mathematical treatment, each of these quantities ($\mathfrak{F}_s$, $\mathfrak{F}_d$, and ζ) will be considered as a variable. Hence, equation 24 is a parabola with the maximum value of $\mathfrak{F}_s$ where $\zeta = 0$. Equation 25 is a straight line the slope of which ($4\ \mathfrak{F}_m\ \gamma\delta$) is positive if δ is positive. Taking derivatives of equations 24 and 25

$$\frac{d\mathfrak{F}_s}{d\zeta} = -4\mathfrak{F}_m\gamma\zeta \tag{26}$$

$$\frac{d\mathfrak{F}_d}{d\zeta} = 4\mathfrak{F}_m\gamma\delta \tag{27}$$

When these derivatives are equal, $\zeta = -\delta$. To find the value of ζ at which the two derivatives are numerically equal, the experimental data obtained for both $\mathfrak{F}_s$ and $\mathfrak{F}_d$ by varying ζ are plotted on the same sheet using the same scale in each plot, but not necessarily with the same origin of coordinates. Typical curves are shown in figure 9. A straight line is drawn parallel to the line representing $\mathfrak{F}_d$ as a function of ζ at such a position that it is tangent to the parabola representing $\mathfrak{F}_s$ as a function of ζ. The value of ζ at the point of tangency gives the value of δ, since at this point the derivative of $\mathfrak{F}_s$ is numerically equal to the derivative of $\mathfrak{F}_d$. In figure 9, the value of δ is given by the distance *bc*.

The same curves can also be used to determine the difference between the computed maximum force $2\mathfrak{F}_m + \epsilon$ and the measured maximum force $\mathfrak{F}_{sm}$. When $\zeta = \pm\delta$, the moving coil is at the position for maximum force with respect to one fixed coil, and at a distance 2δ from the position for the other coil. Substituting the value of ζ in equation 24, the following equations result:

$$\text{When } \pm\zeta = \delta,\ \mathfrak{F}_s = 2\mathfrak{F}_m\,(1 - 2\gamma\delta^2) + \epsilon \tag{28}$$

$$\text{When } \zeta = 0,\ \mathfrak{F}_{sm} = 2\mathfrak{F}_m\,(1 - \gamma\delta^2) + \epsilon \tag{29}$$

Eliminating γ between these equations, and rearranging

$$2\mathfrak{F}_m + \epsilon = \mathfrak{F}_{sm} + (\mathfrak{F}_{sm} - \mathfrak{F}_s) = \mathfrak{F}_{sm} + \Delta\mathfrak{F} \tag{30}$$

The value of $\Delta\mathfrak{F}$ is given by the distance *ab* on the curve of figure 9. The correction $\Delta\mathfrak{F}$ is the amount that must be added to the maximum value of the measured force to obtain the value that would have been measured had the fixed coils been correctly spaced.

The reasoning used above can be applied when the two fixed coils are not exactly coaxial. In this case, the sum of the forces is a mini-

mum when the axis of the moving coil lies midway between the axes of the fixed coils, so that the sign of the correction terms in the force equations is positive instead of negative as given in equations 22 and 23 and hence the sign of $\Delta\mathfrak{F}$ is negative instead of positive. The displacement of the fixed coils from the coaxial position was resolved along two horizontal axes, and corrections applied for each of these axes. The method of finding the amount of displacement and the correction for this displacment is the same along each horizontal axis as the method described for the distance between the coils, i.e., the vertical axis.

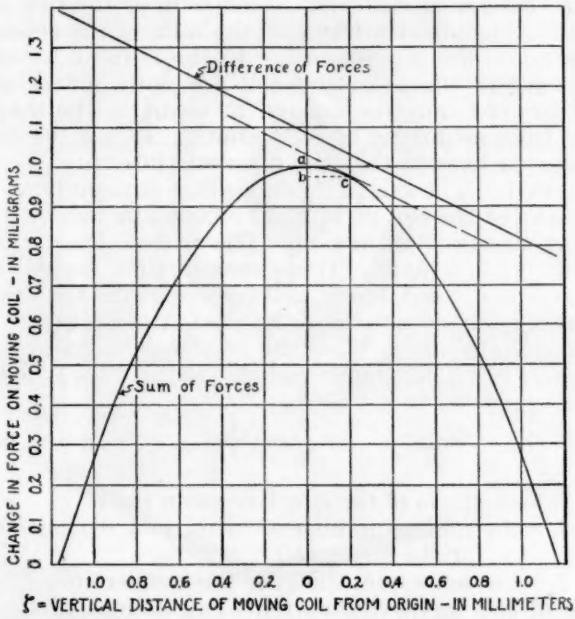
Difference of Forces
Sum of Forces
a
b
c
CHANGE IN FORCE ON MOVING COIL - IN MILLIGRAMS
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3
1.0 0.8 0.6 0.4 0.2 0 0.2 0.4 0.6 0.8 1.0
δ = VERTICAL DISTANCE OF MOVING COIL FROM ORIGIN - IN MILLIMETERS

FIGURE 9.—*Variation of the sum and difference of the forces with vertical displacement of the moving coil. Vertex of the parabola is a, point of tangency of line is c.*

The experimental curve for the sum of the forces was taken with coils S1, S2, M2 with a current of 0.678 amperes, giving a total doubled force of 5.29 grams. The line for the difference of the forces was drawn arbitrarily, as the actual line corresponding to the difference of the forces was too nearly horizontal to make a suitable illustration.

The plotted data would be interpreted as follows: The length *bc* gives the distance, δ (0.2 mm), which each fixed coil would have to be moved to attain perfect spacing and the length *ab* gives the correction, $\Delta\mathfrak{F}$ (0.03 mg), to the doubled force for the assumed incorrect spacing.

V. DETERMINATION OF THE RATIO OF THE RADII OF THE COILS

The theory of the current balance shows that the ratio of the radius of the moving coil to that of each of the fixed coils must be known in order to compute the current from the measured force. These ratios, while very difficult to determine by mechanical measurements, may be very precisely determined by a relatively simple electromagnetic method. This method is based on the fact that the magnetic field at the center of a circular turn of wire is directly proportional to the current in the wire, is inversely proportional to the radius of the circle, and is in a direction perpendicular to the plane

of the circle. If two circular turns are coplanar and concentric, and carry currents flowing in opposite directions, the resultant magnetic field at their common center is zero for a particular value of the ratio of the two currents. When the common plane of the two circular turns is vertical, and in the magnetic meridian, a small magnet hung at the common center of the turns will be undeflected when the field resulting from the currents is zero. With zero field at the center, the ratio of the currents is equal to the ratio of the radii of the turns.

If each circular turn is replaced by a coil having a number of turns and a relatively small cross section, the above procedure may be used to obtain the ratio of the effective mean radii of the two coils. This ratio of the radii is not identical with the ratio of the geometric mean radii but is more directly applicable to the current balance. Since only the magnetic effects of the coil are under consideration, the features of the coil must be defined in terms of the magnetic field rather than from geometric considerations. Hence the plane of the coil is a plane so located that the magnetic intensity is symmetrical with respect to it. The axis of the coil is that straight line perpendicular to the plane of the coil in which the magnetic field at every point has the same direction as the line. The center of a coil is the point where its axis cuts its plane. It is apparent that the plane, axis, and center of a coil, as defined above, will coincide with the same features as geometrically defined, provided the coil is a perfect one.

As a first approximation, when the resulting magnetic field at the common center of two coplanar and concentric coils is zero

$$\alpha \equiv \frac{a_2}{a_1} = \frac{n_2 I_2}{n_1 I_1} \tag{31}$$

where α = the ratio of the effective mean radii

a_1, n_1, I_1 = the radius, number of turns, and current respectively for the larger coil

a_2, n_2, I_2 = the same quantities for the smaller coil.

The ratio of two unvarying currents can be measured with an accuracy of a part in a million, and the number of turns determined with about the same accuracy. However, corrections must be made for the finite cross sections of the coils.

1. OUTLINE OF METHOD [29]

A large coil and a small coil were mounted as nearly concentric and coplanar as feasible, with their common plane vertical and approximately in the earth's magnetic meridian. A small magnet was suspended at the common center. A suitable current was sent through one coil, and the current in the other was varied until the magnetic needle showed no deflection. The ratio of the currents was then measured. The position of one coil relative to the magnet was then changed by a measured amount, the current varied, and the ratio of currents again measured. After three or more such readings, corresponding to a particular type of adjustment, had been obtained, a curve was plotted with positions of the coil as abscissas and ratios of currents as ordinates. The curve was a portion of a parabola, and

[29] The general method was described by Bosscha, Pogg. Ann. vol. 93, p. 392, 1854.

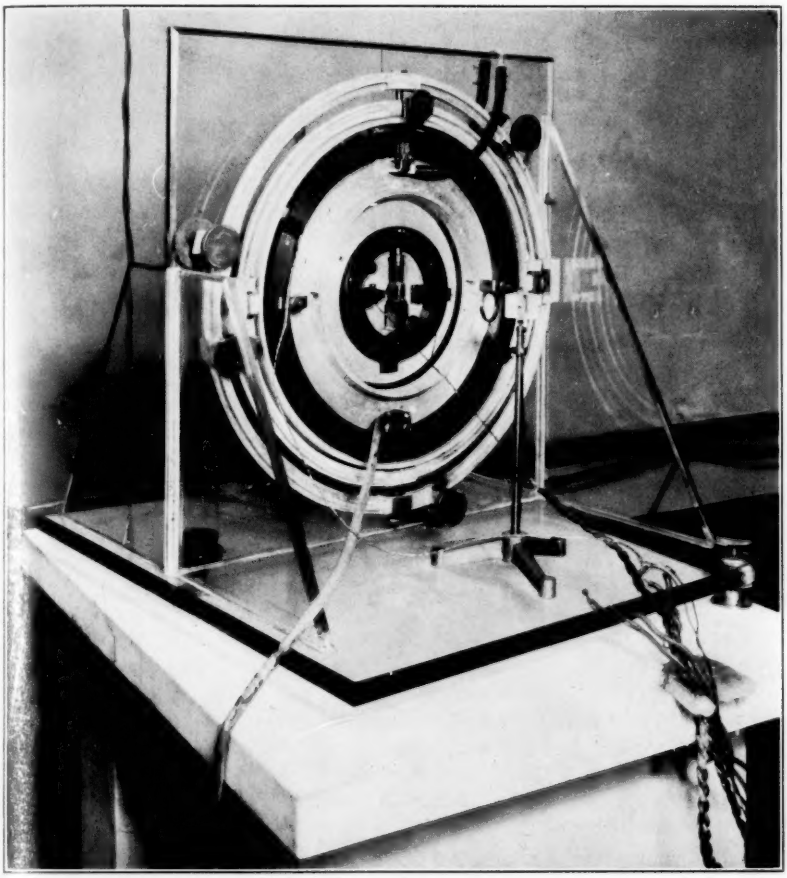

FIGURE 10.—*Photograph showing the way in which two coils were mounted when measuring the ratio of their radii.*

The large coil was held in a double gimbal system by which it could be independently given two rotations and three translations. The small coil was held in a single gimbal by which it could be independently given one rotation and one translation. The magnet could be given one rotation and two translations. The coils could be placed in magnetic meridian by turning the entire stand.

The mountings of the coils and all the connections to them, as well as the tripod stand and all of the optical parts carried by it, were tested by the astatic magnetometer and each piece was accepted only if its magnetic susceptibility differed but little from unity.

UNIV. OF MICH.

the abscissa for maximum or minimum ordinate indicated the correct position for this adjustment. The coil was then placed at the position indicated by the maximum or minimum and a second adjustment made. This procedure was continued for all necessary translations and rotations of each coil. The maximum or minimum point of the final adjustment indicated the point at which the coils were exactly coplanar and concentric with the magnet at the center. Then the product of the ratio of the currents and the ratio of the number of turns gives a first approximation to the ratio of the effective mean radii of the coils. Corrections could then be made for the finite length of the needle and for the cross sections of the coils.

2. MOUNTING OF THE COILS

The stand for holding the coils was constructed of plate glass which was chosen because it was nonmagnetic, could be procured in large pieces, and could be readily cemented together. The large coil was mounted on the glass upright in such a manner that the coil could be given 3 translations and 2 rotations by means of a double gimbal made of an aluminum alloy. The small coil was mounted on an aluminum disk rigidly attached to the glass upright by means of a single brass gimbal in such a way that the coil could be given 1 translation and 1 rotation. All the materials used in connection with the mounting of the coils were tested for their magnetic properties by an astatic magnetometer. (See p. 710.) A photograph of the assembled stand is shown in figure 10.

3. MAGNETOMETER

The magnetometer consisted of an outer case, a suspended system, a fiber for suspending this system, and adjustment screws for raising and lowering the suspended system and for turning it around a vertical axis. The magnetometer was mounted on a slide so attached to the plate glass that the entire magnetometer could be moved in the direction perpendicular to the upright glass plate.

The magnetometer case consisted of a tube of nonmagnetic brass. The tube was closed at the lower end and had a window made of glass having optically flat faces. The moving system consisted of a small glass rod to which was attached a small magnet, a small mirror, and the wing of an insect to act as a damping vane. All parts of the moving system were made with as small a moment of inertia as possible, in order that the period would be short. The size of the damping vane was adjusted until the moving system was slightly under-damped. A quartz fiber was used for suspending the moving system.

4. OPTICAL SYSTEM

The optical system consisted of the conventional lamp and scale in which the light was reflected from the small mirror of the moving system of the magnetometer to a scale 3.7 meters from the mirror. The mirror was mounted in the same plane as the magnet, and the light source was ordinarily placed along the axis of the coils. In some cases readings were required with the magnet deflected about 30° from the plane of the coils. For such readings a second light source was employed, the beam of which made an angle of about 60° with the axis.

5. ELECTRICAL CONNECTIONS

The electrical connections used in determining the ratio of the radii are shown in figure 11. A storage battery controlled by a single switch supplied currents to two parallel circuits, each having a rheostat for adjusting the current and a switch for reversing it. The 2 reversing switches and the battery switch were mechanically connected so that 1 switch handle operated them all. The battery switch opened first and closed last so that the currents in the two coils were broken and made simultaneously. An adjustable iron-cored

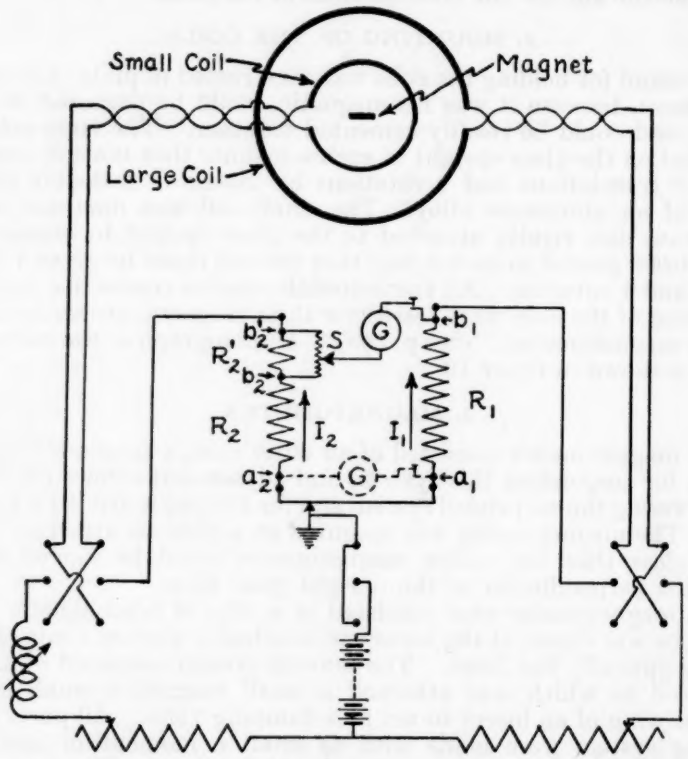

FIGURE 11.—*Electrical circuit used in measuring the ratio of the radii of the coils.*

The currents in the two coils were adjusted until their resultant magnetic field at the common center was zero, as indicated by the zero deflection of the small magnet at the center. The ratio of the two currents could be measured by the circuit shown and the ratio of the radii computed from the ratio of the currents. The two reversing switches and the battery switch were connected together mechanically so that the currents could be quickly reversed.

inductor in the small-coil circuit made the time constants of the two circuits nearly the same. This inductor was placed so far from the coils that its magnetic field did not deflect the magnet by a readable amount. Without this inductor, the magnet received a large deflection when the circuit was opened or closed; with it, the swing was reduced to a few degrees.

Observations were made with the currents in both directions in order to eliminate the effect of slow changes in the zero position of the magnet. In order to measure the ratio of radii with an accuracy

of one part in a million, the deflection of the magnet, with 1 ampere in the small coil, must be observed to 70 microradians or 0.5 mm on the scale.

The zero position of the magnet must not have changed more than this amount during the 10-second interval necessary to make two readings, between which the currents in both coils were reversed. The zero position of the magnet depended almost entirely on the direction of the horizontal component of the external magnetic field, changes in which were caused either by variations in the earth's field or by fluctuations in the current in outside circuits. The most troublesome of the latter was a street-car line which was 300 meters distant. When this line was in operation, the zero of the magnet was not sufficiently steady. Consequently, all ratio-of-radii adjustments and measurements had to be made between the hours of 2:30 and 4:30 a.m., when the street cars were not running. It was not always possible to work even at these hours on account of magnetic storms. While this work was in progress, the daily reports on terrestrial magnetic conditions were received from the Cheltenham Magnetic Observatory and from Science Service; the reports reaching this laboratory several days after the observations were made. It was usually possible to correlate a poor set of results on the ratio of the radii with poor magnetic conditions, thus justifying their rejection.

The ratio of the currents was determined by observing that the potential drop over a resistance carrying a current I_1, was the same as that over another resistance carrying a current I_2. Then the ratio of the currents was equal to the inverse ratio of the two resistances. The arrangement of circuits for making the measurement is shown in figure 11. The battery current divided into the two currents I_1 and I_2 at a terminal which could be adjusted until the potential terminals a_1 and a_2 of the standard resistors were at the same potential. This adjustment was not appreciably altered by other changes in the circuit, so that it had to be made only once or twice during the measurements on a pair of coils. The galvanometer connection could be moved along the slide wire, S, to make the potential of some point between b_2 and b_2' the same as that of the terminal b_1. If the slide wire has s divisions, and if the reading of the slide wire is x, the ratio of currents is given with sufficient accuracy, with the resistances used, by the equation

$$I_1/I_2 = (R_2 + \frac{x}{s} R_2')/R_1 \qquad (32)$$

where R_2 is the resistance between a_2 and b_2; R_2' that between b_2 and b_2', and R_1 that between a_1 and b_1.

The resistor (R_2+R_2') in series with the small coil was usually a 1-ohm standard and carried 1 ampere. A potential tap was taken off at 0.002 ohm and this part of the resistance was shunted by a Kohlrausch slide wire, S, having a resistance of 7.6 ohms. The slide wire had 1,000 divisions, each corresponding to 0.000002 ohm change in the resultant resistance of the resistor so that one half division on the slide wire corresponded to a part in a million in the ratio of the currents.

The standard resistors for use as R_1 and R_2 were constructed from manganin strip in the same manner as those already described for

use with the current balance. They were frequently compared with the primary resistance standards of the Bureau, generally before and after use. They were mounted in an oil bath, which was maintained at or near 25° C; the temperature at which they were tested. However, the current used in determining the ratio of the radii was much larger than the current used in testing. The larger current generated more heat in the resistance material and hence caused a greater temperature difference between this material and the surrounding oil. By means of the load coefficient of the resistance, a correction was applied to the value of the resistance obtained when it was tested to obtain the value of the resistance as used. The load coefficients of the resistors often introduced larger corrections than the temperature coefficients.

A moving-coil galvanometer having a low external critical damping resistance (6 ohms) was used in obtaining the setting of the slidewire. It was mounted so that both the galvanometer and the magnetometer could be read on the same scale. The sensitivity of the galvanometer, when critically damped, was 10 milliradians per microvolt, which gave a deflection of 3 centimeters per microvolt at the scale distance of 3 meters. In order to measure the ratio of the currents to one part in a million, the spot of light from the galvanometer would have to be adjusted only to within 3 centimeters of the correct position.

6. PROCEDURE IN TAKING OBSERVATIONS

In order that thermal conditions would be steady, the current was passed through the coils for several hours before observations were begun. The room was heated electrically, and thermostatically controlled to within 0.2° C. This was necessary because there was no other temperature control for the small coil. Thermostated water, circulating through the large coil, controlled its temperature. Fluctuations in battery voltage did not affect the ratio of currents.

The procedure in making an observation was as follows: The battery switch was momentarily opened to permit the observation of the zero position of the magnetometer; with the switch closed, the current in one of the coils (usually the smaller) was varied until the reading of the magnetometer was the same as the zero position; and almost simultaneously with the variation of the current, the contact on the slidewire was moved until the closing of the galvanometer key did not produce a deflection of the galvanometer. After the reading of the slidewire had been recorded the currents were reversed and the process was repeated. This procedure constituted one observation and took about 10 seconds. Several observations were made for each step in the adjustment of a coil to its correct position, and after the coils had been completely adjusted, about 10 observations were made for the purpose of determining the value of the ratio of the radii. The mean deviation from the mean for 10 observations was seldom as great as one part in a million. The whole arrangement was very sensitive and easily operated by one observer.

7. ADJUSTMENT OF THE COILS AND MAGNET

The adjustment of the coils and magnet was for the purpose of making the coils vertical, coplanar, and concentric, and of placing

the magnet with its center at the common center of the coils and with its axis in the common plane of the coils. The complete adjustment was accomplished by translating and rotating the coils and magnet with respect to a chosen coordinate system and by determining for each translation or rotation (called an individual adjustment) the position at which the ratio of currents was a maximum or minimum, in the manner already described. To determine the number of individual adjustments that must be made, each coil and the magnet may be considered as a rigid body. Since every rigid body has 6 degrees of freedom (3 rotations and 3 translations), the system of 2 coils and a magnet has 18 possible degrees of freedom with respect to a fixed system of coordinates. But the magnetic field of a coil is symmetrical about its axis so that from a magnetic point of view each of the coils has only 5 degrees of freedom. Hence, if the coordinate system is fixed in the magnet, it is evident that only 10 individual adjustments are required for a complete adjustment. This arrangement of coordinates is useful to show the minimum number of individual adjustments that must be made, but is not as suitable as some others for actual application. The most convenient arrangement of coordinates is that in which the origin is at the center of the magnet, one axis vertical, one axis horizontal and parallel to the plane of the small coil, and the third axis perpendicular to the other two. The 10 adjustments relative to these axes are given below:

1. Translation of the *small coil* in a direction perpendicular to its plane until its center lies in a vertical plane through the center of the magnet.
2. Translation of the *small coil* in a vertical direction until its center and the center of the magnet are in a horizontal line.
3. Translation of the *small coil* in a horizontal direction in its plane until its center coincides with the center of the magnet.
4. Translation of the *large coil* in a direction perpendicular to its plane until its center lies in a vertical plane through the center of the magnet.
5. Translation of the *large coil* in a vertical direction until its center and the center of the magnet are in a horizontal line.
6. Translation of the *large coil* in a horizontal direction in its plane until its center coincides with the center of the magnet.
7. Rotation of the *small coil* about a horizontal diameter until its plane is vertical.
8. Rotation of the *large coil* about a horizontal diameter until its plane is vertical.
9. Rotation of the *large coil* about a vertical diameter until its plane coincides with that of the small coil.
10. Rotation of the *magnet* about a vertical line through its center until its axis coincides with the common plane of the coils.

For maximum sensitivity, the axis of the magnet should approximately coincide with the magnetic meridian. In this position there is no torque in the suspending fiber. Sufficient sensitivity was obtained by placing the plane of the small coil approximately in the magnetic meridian by comparison with a compass needle and turning the magnet to coincide approximately with this plane. The latter was accomplished by sending a current of a few milliamperes through the small coil and adjusting the torsion head of the mag-

netometer until a reversal of the current produced an equal and opposite deflection of the magnet.

The plate of glass supporting the coils was placed essentially vertical and in the magnetic meridian, and adjustments 1 to 6 were made by moving the coils in directions perpendicular and parallel to that plate, those directions coinciding quite closely with those previously specified in the catalog of the adjustments. In each case the position of the coil at which the ratio of the currents was a maximum or a minimum was determined, and the coil was placed in that position. The apparatus for making the translations was so designed that the small coil could be given only one translation, namely, in a horizontal line in its plane. Hence, for the purpose of making adjustments 1 and 2 which required other translations of the small coil relative to the coordinate system, the large coil and the magnet were moved as a unit, thus moving the coordinate system and those parts that should remain stationary with respect to it, rather than moving the small coil.

The rotational adjustment of the coils to make their planes vertical (adjustments 7 and 8) was accomplished as follows: With the large coil in a definite position, the ratio of the currents giving zero deflection of the magnet was determined for each of several positions of the small coil as it was rotated about a horizontal diameter. The plane of the small coil was made vertical by placing the coil in the position in which the ratio of the current in the small coil to that in the large coil was a minimum. With the small coil vertical, similar observations were made when the large coil was rotated around a horizontal diameter. In this way, the planes of the two coils were made vertical.

To secure data for adjusting the large coil so that its plane coincided with that of the small coil (adjustment 9), the ratio of the currents which produced zero *deflection* of the magnet was measured for two or more displaced zero *positions* of the magnet. The displacement of the zero position of the magnet was usually accomplished by employing the magnetic field of an auxiliary coil, the axis of which approximately coincided with those of the other coils and the center of which was at a distance of 50 cm or more from the center of the coils. By reversing the current in this auxiliary coil, two displaced zero positions of the magnet were obtained which were about equally spaced (usually 2 centiradians, or about 1°) on each side of the initial zero position. By plotting, as ordinates, the slide-wire readings, which were proportional to the ratio of the currents, and, as abscissas, the displaced zero positions of the magnet as read on the scale, a line was obtained, the slope of which was proportional to the angle between the two coils.

Data for determining the proportionality factor between the slope of the plotted line and the angle between the coils was obtained by first turning the large coil around a vertical diameter by a known angle of 1 or 2 centiradians and then making a second set of measurements of the ratio of the currents at two or more displaced zero positions of the magnet. The results were plotted on the same sheet as the first set. The dashed lines in figure 12 show a typical plot of the first two sets of measurements made in the adjustment of a pair of coils. Since, for each line, the slope was proportional to the angle between the coils, the difference in the slopes of the two lines

was proportional to the angle through which the large coil was turned, so that the angle required to turn the large coil to make the two coils parallel was determined by proportion.

The rotation of the magnet to place its axis in the plane of the coils (adjustment 10) would have been unnecessary if the preceding adjustment of the large coil into the plane of the small coil could have been made perfectly. Since this ideal condition could not be

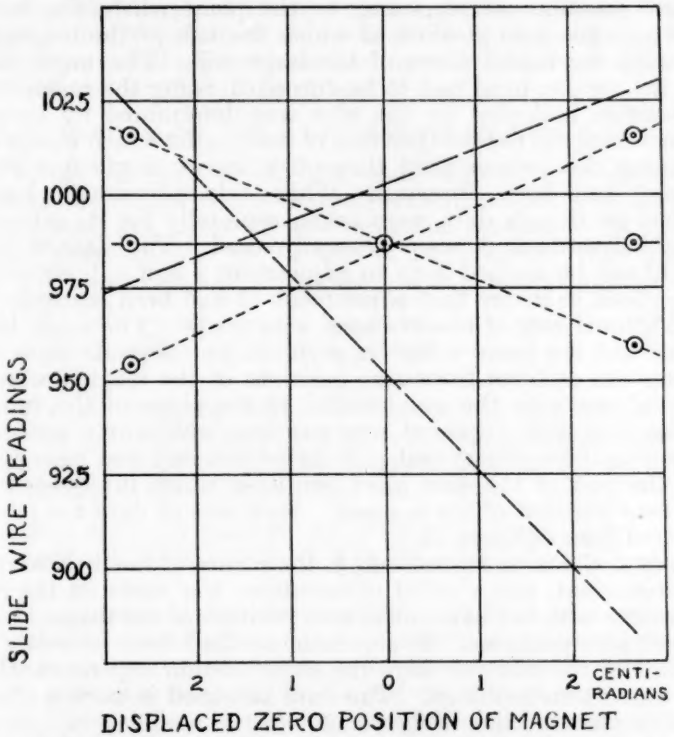

FIGURE 12.—*Data used in turning the plane of the large coil and the axis of the magnet into the plane of the small coil*

The ordinates are slide-wire divisions, each of which is approximately equal to a part in a million in the ratio of the currents. The abscissas are angular positions of the magnet which are measured from the initial zero position. The angle between any line and the horizontal is proportional to the angle between the coils at the time the observations used in plotting the line were made. The horizontal distance between zero and the intersection of two lines, plotted from data taken with the same initial zero of the magnet but with different angles between the coils, is proportional to the angle between the axis of the undeflected magnet and the plane that bisects the angle between the two positions of the plane of the fixed coil.

The dashed lines represent the first set of measurements for determining the angle between the coils and the angular position of the magnet. The coils used in this case were S2 and M3 and the angle between them was 1 milliradian (3.6′). The solid line is from actual data taken on the same coils to check the parallelism after adjustment.

attained, an adjustment of the magnet was always made, for the effect of an error in the adjustment of the planes of the coils to coincidence was minimized if the axis of the magnet was ajdusted nearly to coincide with the plane of the large coil. Such coincidence could not be satisfactorily secured by the approximate method used in setting the magnet before starting any of the adjustments. It was secured by the following procedure: The large coil was turned through

a small angle (1 or 2 centiradians) from the position where it was left in adjustment 9, and the ratio of currents was determined for two or more displaced zero positions of the magnet, as in the previous adjustment. The large coil was then turned by the same amount in the opposite direction. The ratio of currents was again determined for two or more displaced zero positions of the magnet. The data were then plotted as before with slide-wire readings as ordinates and zero positions of the magnet as abscissas, giving two straight lines. The zero position corresponding to the point where the two lines crossed was the zero position at which the axis of the magnet coincided with the initial plane of the large coil. The angle through which the torsion head had to be turned to bring the magnet to the zero position indicated by the plot was determined by proportion after the change in the zero position of the magnet which was produced by turning the torsion head through a known angle (generally 10 divisions) had been observed. While this adjustment has been described as though data were taken especially for it, actually the data of adjustment 9 were generally used. The dashed lines of figure 12 can be applied both to adjustment 9 and adjustment 10.

As a check to insure that adjustment 10 had been correctly made, two additional sets of observations were made. The angle between the coils had the same value for each set, but opposite signs for the two sets. In each set three zero positions of the magnet were used, the initial one with the axis parallel to the plane of the small coil, the other two with displaced zero positions which were produced by a current in the auxiliary coil. If the adjustment had been correctly made, the plot of the data gave two lines which intersected at the initial zero position of the magnet. Such sets of data are plotted in the dotted lines of figure 12.

As a final check on adjustment 9, the planes of the coils were again made coincident, and a set of observations was made on the ratio of the currents with the new initial zero position of the magnet and two displaced zero positions. If adjustment 9 had been correctly made, the ratios of the currents were the same (within experimental error) for all three zero positions. The data obtained in such a check are plotted in the solid line of figure 12.

The above methods do not exactly conform to the conditions stated in describing the necessary adjustments. Hence, after the first series of 10 adjustments had been completed, an entirely new series was made to obtain a closer approximation to the theoretically correct position. In the second series, the positions of the coils and of the magnet were not changed from those in which they were placed by the first adjustment, except as required in making each individual adjustment. If, in the second series, any adjustment was changed by an appreciable amount, a third series was made. After the coils were in perfect adjustment, several careful determinations of the ratio of the currents which produced no deflection of the magnet were made. Since this ratio of currents was used to compute the ratio of the radii of the coils, all necessary precautions were taken to insure an accurate value of the ratio of the currents. This required a procedure somewhat different from that used in the adjustment of the coils, since in those measurements only changes in the ratio of the currents were required. The various measurements of the ratio of the currents for each pair of coils, when in perfect adjustment, were made at different times, but

always with the external conditions approximately those under which the coils would be used in the current balance. Some measurements were usually made just after the complete adjustment had been finished, then additional ones both after the measurement of the temperature coefficient and of the load coefficient and still others after the length of the magnet had been determined.

Under favorable conditions about an hour was required to make an individual adjustment. Since it was possible to work only 2 hours a day, each series of 10 adjustments required about a week. A determination of the ratio of the radii of two coils, consisting of 2 or 3 series of individual adjustments and several final determinations of the ratio of the currents, took at least 2 weeks.

8. THEORY OF THE ADJUSTMENT OF THE COILS

The theory of each of the individual adjustments of the coils depends on the change which that adjustment produces in the torque on the magnet, and hence on the horizontal component of the magnetic field perpendicular to the axis of the magnet. The magnetic field of a coil along its axis is expressed with sufficient approximation by the equation

$$H_z=\frac{2\pi nI}{a}\left[1-\frac{3}{2}\frac{z^2}{a^2}+\ .\ .\ .\ .\right] \tag{33}$$

Where H_z is the magnetic field at a distance z along the axis from the center of the coil, a is the radius of the coil, n the number of turns, and I the current in each turn. The magnetic field in the plane of the coil, H_x (or H_y) is given by the equation

$$H_z=\frac{2\pi nI}{a}\left[1+\frac{3}{4}\frac{x^2}{a^2}+\ .\ .\ .\ .\right] \tag{34}$$

These equations show that the translational adjustments when made with respect to the coordinate axes as described, place the centers of the coils at the center of the magnet. The equations show that an error of a part in a thousand in x/a and z/a will produce an error of only a part in a million in the magnetic field. The smallest coil used had a radius of 10 cm, so that with it a maladjustment of 0.1 mm was permissible. This accuracy was easily attained.

The torque that a coil carrying a current exerts on a magnet suspended at the center of the coil is proportional to the cosine of the angle which the plane of the coil makes with the vertical, and hence is a maximum when the coil is vertical. The adjustment of each coil to be vertical could be made with ample precision, since the cosine does not change appreciably for small angles.

The theory of the adjustment of the coils to have coincident planes by the rotation of one of them around a vertical axis requires that the torques, around a vertical axis, which the magnetic fields of the two coils exert on the magnet shall be equal and opposite. To simplify the equations for the torques, the magnet is assumed to be so short that, at its poles, the magnetic field of each coil is the same as that at its center. The current I_1 in the large coil (radius a_1, number of turns of wire n_1) produces, on the magnet, a torque T_1, which is given by the equation

$$T_1=\frac{2mln_1I_1\cos\ (\phi_m-\phi_c)}{a_1} \tag{35}$$

where l is the effective length of the magnet, m its pole strength, ϕ_m the angle which the magnet makes with the plane of the small coil and ϕ_c the angle between the two coils. (See fig. 13.)

A current I_2 in the small coil (radius a_2, number of turns of wire n_2) produces, on the magnet, a torque T_2 which is represented by the equation

$$T_2=\frac{2mln_2I_2\cos\phi_m}{a_2} \tag{36}$$

Equating the torques, and rearranging

$$\frac{a_2}{a_1}=\frac{I_2n_2\cos\phi_m}{I_1n_1\cos(\phi_m-\phi_c)} \tag{37}$$

It follows from this equation that the ratio of the radii is equal to the ratio of the current-turns if $\cos\phi_m=\cos(\phi_m-\phi_c)$, which is the

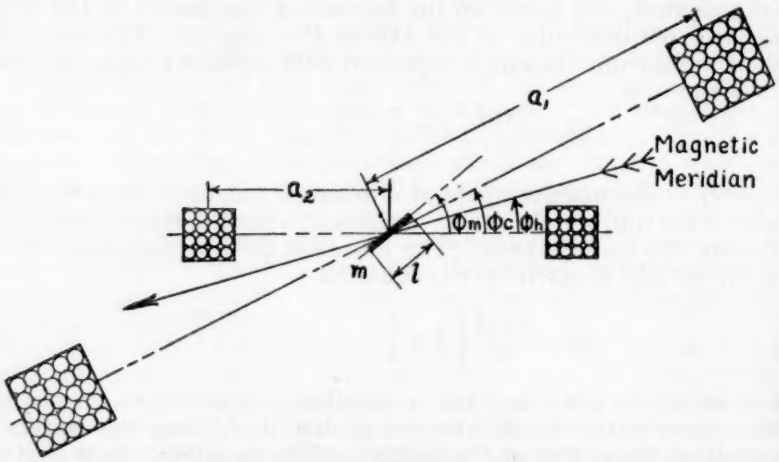

FIGURE 13.—*Horizontal crosssection of the coils and magnet as mounted for measuring the ratio of the radii*

The diagram shows the symbols used in describing the method for adjusting the coils to be coplanar with the axis of the magnet in the common plane.

case when $\phi_c=0$ (the planes of the coils coincident) or when $\phi_m=\phi_c/2$ (the magnet bisects the angle between the planes).

In general, a small error in setting ϕ_c to zero is likely to occur. However, equation 37 shows that the effect of this error may be minimized by making ϕ_m small. For example, if $\phi_m=0$, a value of ϕ_c of 1.4 milliradians (5′) introduces an error in the ratio of the radii of one part in a million but if $\phi_m=2$ centiradians (1°) then this same value of ϕ_c introduces an error of 29 parts in a million.

Equation 37 can be written as

$$\frac{I_2}{I_1}=\frac{n_1a_2}{n_2a_1}(\cos\phi_c+\sin\phi_c\tan\phi_m) \tag{38}$$

Considering ϕ_c as a constant, this is a linear equation between I_2/I_1 and $\tan\phi_m$, in which $\sin\phi_c$, and hence for small angles ϕ_c, is proportional to the slope of the line. This shows the validity of the method employed to adjust the planes of the coils to coincidence.

The equations connected with the above-described adjustment for placing the magnet in the plane of the coils can be obtained from equation 38 by assuming that after the completion of adjustment 9, there is a very small angle, ϵ, between the planes of the coils so that instead of $\phi_c=0$, $\phi_c=\epsilon$. Then with the large coil turned from this position by $+\theta$, equation 38 may be written in the form

$$\frac{I_2}{I_1}=\frac{n_1a_2}{n_2a_1}\left\{\cos\ (\epsilon+\theta)+\sin\ (\epsilon+\theta)\ \tan\ \phi_m\right\} \tag{39}$$

Likewise, when the large coil is turned through an angle $-\theta$

$$\frac{I_2}{I_1}=\frac{n_1a_2}{n_2a_1}\left\{\cos\ (\epsilon-\theta)+\sin\ (\epsilon-\theta)\ \tan\ \phi_m\right\} \tag{40}$$

These equations can be solved to determine the point of intersection of the lines which they represent. Equating the right-hand sides of the equations 39 and 40 and simplifying

$$\tan\ \epsilon=\tan\ \phi_m \tag{41}$$

Hence, when the magnet is adjusted by this method, it lies in the plane of the adjusted large coil and makes an angle ϵ with the plane of the small coil. It follows that equation 37 becomes

$$\frac{a_2}{a_1}=\frac{I_2n_2\cos\ \epsilon}{I_1n_1} \tag{42}$$

However, ϵ is a very small angle, much smaller than the allowable value of the angle ϕ_m. It follows in making this adjustment that ϵ may be considered as zero. In fact, changes in the earth's field may at any time change ϕ_m by an angle larger than ϵ, but such changes were not sufficiently large to affect the value obtained for the ratio of the radii.

The value of ϕ_m was measured by readings on the magnetometer scale. By turning the torsion head through x divisions, the reading on the magnetometer scale was changed by y divisions. Hence, the number of divisions through which the torsion head had to be turned to make the axis of the magnet coincide with the plane of the large coil was $\phi_m x/y$.

9. TEMPERATURE COEFFICIENT OF EXPANSION

The termperature coefficient of expansion was determined experimentally for each coil, since so many elements entered that it could not be computed from the coefficients of expansion of the component parts. The method employed was to measure the ratio of the radii of two coils, one of which was kept at a constant temperature, while that of the other was varied. In the case of the large coils, the change in temperature was accomplished by changing the temperature of the water circulating through the coil forms. The temperature change was usually from about 7° C above to 5° C below the usual room temperature of 22 C. In the case of the small coils, the temperature was changed by changing the temperature of the air in the room. In each case the temperature of a coil was determined by measuring the resistance of the windings and assuming that the temperature coefficient of resistance of the copper winding was 0.0039 per degree centi-

grade. The results of these measurements, as well as those obtained in 1911, are given in table 3.

TABLE 3.—*Temperature coefficient of expansion of the coils*

[Values expressed as relative change in radius per degree centigrade]

Coil	1911 values	1933 values (average)	Maximum variation in 1933 values	Number of determinations in 1933
M2	20.3×10^{-6}	18.9×10^{-6}	0.2×10^{-6}	2
M3	19.7	16.4	.5	7
S1	17.0	17.0	.1	2
S2	17.6	17.4	.2	2
L3	18.9	17.6	.2	2
L4	18.5	18.9	.3	2

In a few cases the difference between the 1911 values and the corresponding 1933 values are somewhat larger than the experimental errors of the determinations.

The coils were somewhat constrained by their mountings, so that their expansion might have been influenced thereby. To test this effect, a special mounting was made for coil M3 using the hole-slot-plane system so that the coil could expand without constraint. The temperature coefficient with this special mounting was the same as with the regular mounting.

10. LOAD COEFFICIENT OF EXPANSION

The load coefficient of expansion of a coil is the relative change in radius for unit change in load (a power of 1 watt continuously transformed into heat) the temperature of the windings being the same in both cases. The load correction is required because, in most coils, the radius of the windings is, to some extent, affected by the radius of the form. If the wire of the windings is under tension, and if the temperature of the winding is higher than the temperature of the form, an increase in the temperature of the form only to make it equal to that of the winding will increase the tension in the winding and increase its radius. The load on a coil causes the temperature of the windings to be higher than the temperature of the form. Since the temperature of the winding only is determined by measuring its resistance, the radius of a coil which is carrying current and which has tension in the wire of the winding is less than would be the case if the form were at the temperature of the winding. Hence the correct radius of the winding is obtained by subtracting from the radius, as determined when the winding and form have the same temperature, a quantity which is proportional to the load that is converted into heat in the windings. The proportionality factor by which the load must be multiplied is called the load coefficient.

The method of measuring the load coefficient made use of the fact that each coil had 2 identical windings. When the 2 windings of a coil carried equal currents but in opposite directions, there was no magnetic field at the center of the coil, whereas if the 2 currents were in the same direction, the magnetic field was twice that for a single winding. Accordingly, a circuit was arranged so that the current

ordinarily used in measuring the ratio of radii flowed as usual, i.e., produced a field at the center of the coil, while a special heating current flowed through the windings in such a way as to produce no magnetic field at the center. The circuit in figure 14, which is a Wheatstone bridge circuit, shows the way in which this was accomplished. In setting up this arrangement a galvanometer was first connected in place of the heating battery and the circuit balanced as an ordinary Wheatstone bridge by varying either of the resistances P or Q (about 12 ohms each). Later a better balance was obtained with the magnetometer itself, this being done by disconnecting the main battery and adjusting the resistance P (or Q) until the magnetometer zero was not changed when the heating battery was connected. The resistances R_a and R_b (usually 1 or 5 ohms) were inserted so that the current through each winding (and hence the total load) could be determined by measuring the fall in potential over them. Temperature measurements of each winding were made by comparing the fall in potential over the windings with the fall in potential over the resistance standards carrying the same current. Care was taken to have the heating battery well insulated from the main battery.

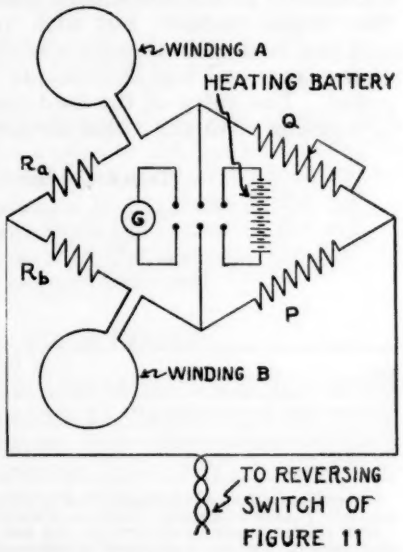

FIGURE 14.—*Auxiliary electrical circuit used for measuring the load coefficient of a coil.*

The auxiliary circuit was used in connection with the measurement of the ratio of the radii and was substituted for the regular circuit of the coil being studied at the reversing switch shown in figure 11. The 2 windings A and B are shown separately, whereas in figure 11 they are considered as a single winding. The total load on the windings was varied by changing the voltage of the heating battery.

The currents in the 2 windings were not the same during these measurements and hence the 2 windings carried different loads. In the special case where the voltage of the heating battery was adjusted so that the heating current and the measuring current were equal, 1 winding carried all the current and the other carried none. Careful temperature measurements on the 2 windings when there was a considerable difference in load gave no indication that 1 winding was at a different temperature from the other. The total load on the coil was always taken as the sum of the loads of the 2 windings.

In making a determination of the ratio of the radii, the temperature and load of 1 coil was kept constant, while the heating current on the other coil was varied from zero to the maximum permissible. The observed relative increase in diameter when the load was increased was subtracted from the relative increase which would have occurred if the form had also been raised to the temperature of the winding (this latter was computed from the temperature coefficient) and the remainder was divided by the load in watts to obtain the load coefficient.

For the large coils the load coefficients were small, and could be determined with sufficient accuracy by this method although the normal loads on them when used in the current balance were large (20 to 50 watts) so that the load corrections were appreciable. For the small coils the load coefficients were large so that the load corrections were appreciable although the normal loads when used in the current balance were small (1 or 2 watts). Moreover, the determination of the load coefficients was difficult, since the normal loads when measuring the ratio of the radii were nearly as large as the coils could safely carry. The above-described method was used with the small coils, but a more convenient method of obtaining the load coefficients of the small coils was to measure the ratio of the radii in the regular manner, but with various measuring currents. In this way the load on both coils was changed, but since the load coefficient of the large coil was known, the one for the small coil could be computed. The value of the load coefficient of each coil is given in table 4, together with the value obtained in 1911.

TABLE 4.—*Load coefficients of the coils*

Coil	1911 value	1933		
		Value	Average deviation from mean	Number of determinations
M2	2.9×10^{-6}	3.3×10^{-6}	0.1	2
M3	8.2	[a]1.0	1.0	6
S1	.47	[b].61	.11	3
S2	.93	[b].52	.16	5
L3	.81	[b].62	.14	3
L4	.84	[b].66	.26	6

[a] The values of the load coefficient of coil M3 had wide variations which were partly caused by the large uncertainty in the temperature coefficient of this coil. (See table 3.)
Both the temperature coefficient and the load coefficient of this coil have decreased since the 1911 measurement. This can be explained by assuming that the winding strains have been relieved.

[b] The load coefficients of the large coils were measured with about 1.2 liters of water per minute flowing through them. No measurements were made to determine whether the rate of flow affected the load coefficient, but this same rate of flow was used when the coils were mounted in the current balance.

In the case of the moving coils, where the load coefficient was the most uncertain, the effect of an error in it on the absolute value of the current was reduced by using the same value of the current in the measuring circuit of the ratio of the radii set-up as was later used in the current balance circuit.

The temperature coefficient and the load coefficient are related to the radius of a coil by the following equation:

$$a_0 = a\{1 - \tau\ (t - 22\ \text{C}) + \psi p\} \tag{43}$$

where

τ = temperature coefficient
ψ = load coefficient
p = load in watts
t = temperature of winding measured electrically
a_0 = radius of coil at 22 C and no load
a = radius of coil at temperature t and load p

In this equation the standard conditions are taken as 22 C and zero load.

11. CORRECTION FOR THE LENGTH OF THE MAGNET

A correction to the observed ratio of the radii for the length of the magnet was required, because the components of the magnetic fields that were perpendicular to the magnet at its poles and hence which must be equal and opposite in order that the magnet should not be deflected, do not have the same ratio as the magnetic fields at the common center of the coils and magnet. The magnetic field produced by a current in a circular coil can be obtained at any point by differentiating the formula for magnetic potential [30] at that point. Near the center of a coil, the differentiation to give the component which is perpendicular to a line through the center of the coil at a given distance from the center and which lies in a plane that is perpendicular to the plane of the coil results in the equation

$$H_\theta = -\frac{d\Omega}{rd\theta} = \frac{2\pi n I \sin\theta}{a}\left[1 - \frac{3}{4}\frac{r^2}{a^2}(5\cos^2\theta - 1) + \cdots\right] \qquad (44)$$

where H_θ = the component of the magnetic intensity at the point (r, θ) which is at right angles to the line connecting the point (r, θ) to the center of the coil and which lies in a plane that is perpendicular to the plane of the coil
r = the distance of the point from the center of the coil
θ = the angle between the axis of the coil and the line connecting (r, θ) to the center of the coil
a = the radius of the coil
n = the number of turns of wire in the coil
I = the current through the coil

If a magnet, the distance between the poles of which is $2r$, is suspended by a fiber with the center of the magnet at the center of the vertical coil, H_θ is the component of the magnetic field which tends to turn the magnet around the fiber. If the magnetic fields of two concentric and coaxial coils are equal and opposite at the poles of the magnet, it follows from equation 44 that

$$\left(\frac{I_2}{I_1}\right)_\theta = \frac{a_2 n_1}{a_1 n_2}\left[1 + \frac{3r^2}{4}\left(\frac{1}{a_2^2} - \frac{1}{a_1^2}\right)(5\cos^2\theta - 1) - \cdots\cdots\right] \qquad (45)$$

where $\left(\frac{I_2}{I_1}\right)_\theta$ is the ratio of the currents which produce no deflection of the magnet when it makes an initial angle θ with the common plane of the coils. The second term in the brackets is the correction which must be applied on account of the length of the magnet. If $5\cos^2\theta = 1$, the correction term is zero, but this requires an angle ($\theta = 63°26'$) that is not convenient for regular use. Observations were regularly made with $\theta = 90°$, in which case the ratio of the radii was computed from the ratio of the currents by the equation

$$\left(\frac{I_2}{I_1}\right)_{90°} = \frac{a_2 n_1}{a_1 n_2}\left[1 - \frac{3r^2}{4}\left(\frac{1}{a_2^2} - \frac{1}{a_1^2}\right) - \cdots\cdots\right] \qquad (46)$$

in which the length of the magnet is required. The length of the magnet was determined by measuring the ratio of currents for two

[30] Maxwell, Electricity and Magnetism, 3d ed., vol. 2, p. 334, eq. 8. Oxford University Press.

markedly different values of θ. Substituting the two sets of values in equation 45, subtracting the resulting equations, and solving for r, the following equation is obtained:

$$r^2=\frac{4}{15}\frac{n_2a_1}{n_1a_2}\left\{\frac{a_1^2a_2^2}{a_1^2-a_2^2}\left[\left(\frac{I_2}{I_1}\right)_{\theta_1}-\left(\frac{I_2}{I_1}\right)_{\theta_2}\right]\frac{1}{\cos^2\theta_1-\cos^2\theta_2}\right\} \quad (47)$$

The values of θ_1 and θ_2 were generally about 60° and 90°.

In the above theory, the assumption has been made that the coils were in perfect adjustment. Slight errors in certain of the adjustments had a very pronounced effect on the measured length of the magnet. The length of the magnet was always measured with at least two pairs of coils. Such measurements were a check not only on the length of the magnet but also on the perfection of the adjustment of the coils.

As the value of the correction term increases as the square of the length of the magnet, r, the magnet should be made as short as possible. The smallest magnet used was about 1.4 mm long. With it, a change in the ratio of the currents of a part in a million could be readily measured.

Four different magnets were employed in the course of this investigation. They were made of cobalt magnet steel and given a special heat treatment. All of them were 0.86 mm wide and 0.24 mm thick, and they varied in length from 1.41 mm to 2.95 mm. The effective length (distance between poles) of each of these magnets has been measured by the method outlined above. The ratios of the effective length to the actual length of these magnets are given in table 5. These ratios agree well with those obtained in 1911, when the method was developed.

Table 5 also gives the corrections to the ratios of the radii which had to be made on account of the lengths of the magnets. The advantage in using short magnets is clearly shown. Although the effective length of a small magnet can not be determined with the same relative accuracy as that of the longer magnets, yet the correction for the shorter magnets is so much smaller that it is advantageous to use them in the determinations of the ratio of the radii.

TABLE 5.—*Lengths of the magnets, and the resulting corrections to the measured ratio of the radii for the different pairs of coils*

Actual length	Ratio of effective to actual length	Correction to the measured ratio of radii			
		Pairs S1 M2 and S2 M2	Pairs S1 M3 and S2 M3	Pairs L3 M2 and L4 M2	Pairs L3 M3 and L4 M3
mm					
1.41	0.80±0.014	9×10^{-6}	18×10^{-6}	11×10^{-6}	20×10^{-6}
1.80	.80± .002	15	29	19	33
2.20	.84± .001	25	48	31	54
2.95	.86± .005	47	91	58	101

For three pairs of coils, determinations of the ratio of the radii were made with magnets of different lengths. The results, given in table 6, are affected by all the errors of a determination, since the

coils had to be readjusted whenever the magnet was changed. The values used in the final computation were those measured with the shorter magnets, since with them the chance of an error was smaller.

TABLE 6.—*Ratio of radii of coils as measured with magnets of different lengths*

Date	Coils	Length of magnet	Correction	Number of observations in set	Ratio of radii	Average deviation from mean of set
1931		*mm*				
July	M3:S2	2.95	91×10^{-6}	4	[a] 0.5(1.005038)	3×10^{-6}
August	do	2.95	91	4	[a] .5(1.005059)	2
October	do	2.21	48	5	[a] .5(1.005040)	2
February–March	do	1.80	29	8	[b] .5(1.005022)	2
September	do	1.80	29	11	[a] .5(1.005037)	2
November	M3:L4	2.21	54	8	.4(1.003259)	5
1932						
January	do	2.21	54	4	.4(1.003266)	1
March	do	1.41	20	8	.4(1.003258)	1
January	M3:L3	2.21	54	10	.4(1.003444)	2
February	do	1.41	20	8	.4(1.003440)	1

[a] These results were obtained when the temperatures were high, a condition unfavorable for precise electrical measurements. Also, one of the resistance coils was changing erratically with time, making these results somewhat uncertain.

[b] This result was obtained in the winter, soon after the coils were used in the current balance and is the one used in the final computations.

12. CORRECTION FOR THE SECTIONAL DIMENSIONS OF THE COILS

The correction for the sectional dimensions arises from the fact that the magnetic field at the center of a coil carrying a current is not the same as if the current were concentrated in a filament located at the center of the cross section of the coil. The field at the center of a coil of rectangular cross section can be determined by the equation [31]

$$H=\frac{2\pi nI}{a}\left(1-\frac{b^2}{2a^2}+\frac{c^2}{3a^2}+\frac{3b^4}{8a^4}+\frac{c^4}{5a^4}-\frac{b^2c^2}{a^4}+\cdots\cdots\right) \qquad (48)$$

$$=\frac{2\pi nI}{a}(1-\Delta)$$

where n = number of turns in the coil
I = current in each turn of the coil
$2b$ = axial dimension of the cross section of the coil
$2c$ = radial dimension of the cross section
a = mean radius of the coil
Δ = correction for reducing the magnetic field of a coil of rectangular cross section to that of a filament having a radius equal to the mean radius of the coil

The values of Δ are given for each coil in table 7, together with the values of a, b, and c, repeated from table 1, as measured when the coils were originally wound.

[31] See p. 314 of paper by Rosa, Dorsey, and Miller, reference footnote 8, or eq. 24 of Snow's paper, reference footnote 25.

TABLE 7.—*Corrections to the magnetic fields at the centers of the coils for their finite cross section*

Coil	a	$2b$	$2c$	Δ*
	cm	*cm*	*cm*	
M2	12.499	0.956	0.955	246×10^{-4}
M3	10.030	.997	1.029	359
S1	19.97	1.580	1.528	295
S2	19.96	1.579	1.522	298
L3	25.00	1.969	1.943	273
L4	25.00	1.965	1.925	279

* The values of Δ in this table were obtained from table VI of the paper by Rosa, Dorsey, and Miller (reference footnote 8) by subtracting the numbers in the last column from unity.

In deriving equation 48 the assumption has been made that the turns of wire in each layer are equally spaced and that corresponding turns in the different layers lie in planes which are perpendicular to the axis of the coil. The axial dimension of such a coil is equal to the number of turns per layer multiplied by the distance between the centers of the turns. If the wires are equally spaced and if the width of the channel in which they are wound is greater than the product of the number of turns per layer by the diameter of the wires, the axial dimension, $2b$, may be greater or less than the width of the channel in which the coil is wound. In an actual coil it is generally impossible to determine the value that should be taken. However, the corrections for cross section have all been computed on the assumption that the width of the winding channel is equal to the axial dimension of the coil. In the same way the radial dimension, $2c$, is equal to the number of layers multiplied by the distance between the layers. The distance between layers was measured at the time of the winding of the coils, and the average value was used in determining the radial dimension. Hence the radial depth, $2c$, of the coils has been determined as nearly as possible to correspond with the method required by theory.

If the magnetic fields of two coaxial coils are equal and opposite at their common center, the ratio of the radii, α, is given by the equation

$$\alpha \equiv \frac{a_2}{a_1} = \frac{n_2 I_2}{n_1 I_1}(1+\Delta_1-\Delta_2) \tag{49}$$

As the value of Δ for M2 is smaller than for any of the fixed coils, the correction term was always positive when M2 was being used. On the other hand, Δ for M3 is larger than for any of the fixed coils, so with this coil the correction was negative.

13. EFFECT OF THE LEADS

The correction for the leads to the coils was found by disconnecting the windings, short circuiting the leads with drops of solder (see fig. 3), and measuring the magnetometer deflection for normal current through the leads alone. Since the sensitivity of the magnetometer was known, the lead correction could be computed. It was always small, but measurable.

14. SOURCE OF ERROR

The most important sources of error in the determinations of the ratio of the radii were the following: (1) Error caused by maladjustment of the coils; (2) errors in temperature corrections; (3) errors in load corrections; (4) errors in the corrections for sectional dimensions; (5) errors caused by magnetization of the forms; and (6) errors in electrical measurements.

Each of these errors will now be separately discussed, and an estimate made of the effect of each error on the ratio of the radii.

(1) The error in the measured ratio of the radii of any pair of coils caused by their maladjustment was small. The series of individual adjustments was repeated until each individual adjustment agreed with that of the preceding series. After a complete adjustment had been made, a check was obtained in connection with the measurement of the effective length of the magnet. Lack of perfect adjustment probably did not in any case affect the measured value of the ratio of the radii by as much as two parts in a million.

(2) The error in the temperature correction, i.e., the error in reducing the ratio of radii from the measured temperature to the standard temperature, resulted from uncertainties in the measured temperature of the winding and from inaccuracies in the value of the temperature coefficient. The temperature of the winding was obtained by comparing the potential drop across it with the potential drop across a standard of resistance connected in series, and could be measured to 0.02° C. The temperature coefficient was known to about 1 percent. Hence the error in reducing the ratio of the radii to standard temperature for temperature differences less than 7° C (the maximum observed) was probably less than three parts in a million for each pair of coils.

(3) The error in the load correction was caused entirely by uncertainties in the load coefficient which have already been discussed. A consideration of all the factors involved has led the authors to the opinion that the error in the ratio of the radii caused by the load correction was not more than two parts in a million for any pair of coils.

(4) The error in the corrections for determining the radius of the equivalent filament from the cross-sectional dimensions of the coils depended on uncertainties in the values of the depth and the breadth of the coil. A formula for determining the error in the ratio of the radii from the errors in the dimensions of the coils can be obtained by differentiating equation 49. If terms of higher order than the second are neglected, the resulting equation is

$$\frac{\delta\alpha}{\alpha}=\frac{b_1^2}{a_1^2}\frac{\delta b_1}{b_1}-\frac{2}{3}\frac{c_1^2}{a_1^2}\frac{\delta c_1}{c_1}-\frac{b_2^2}{a_2^2}\frac{\delta b_2}{b_2}+\frac{2}{3}\frac{c_2^2}{a_2^2}\frac{\delta c_2}{c_2} \tag{50}$$

If the error in any cross-sectional dimension is assumed to be 0.001 cm, the resulting error in the ratio of the radii is in no case more than three parts in a million for any pair of coils used in this investigation; for most pairs it is nearer one part in a million.

(5) The error caused by any magnetization of the forms was very difficult to estimate. In 1911 there were used two sets of fixed coils,

which were of the same size, but one of which (L1 L2) was about 100 times as magnetic as the other (L3 L4). The same result was obtained with both sets. The set L1 L2 has not been used in the present investigation.

A simple and convenient instrument for comparing the magnetic properties of the coil forms and of miscellaneous materials is a small astatic magnetometer. Such an instrument having one of the small magnets of the moving system about 2 inches below the other, was arranged with a series of mirrors in the optical system so that the operator could put the material close to one of magnets and at the same time watch the spot of light on the scale. All materials used in the construction of the current balance and the apparatus for determining the ratio of the radii were tested by this instrument. It was often difficult to get brass which would not cause a deflection of a few centimeters, but, by selection, stock brass could always be found that did not give a deflection greater than a few millimeters. This was, somewhat arbitrarily, considered satisfactory since coil L1, which gave a deflection of about 100 cm, had, in 1911, produced a negligible error in the result. A method for the production of non-magnetic brass castings has been developed by the Department of Terrestrial Magnetism of the Carnegie Institution [32] of Washington and has been found to be very useful for this work. The magnetic properties of the materials probably affected the final result by less than a part in a million.

(6) The error caused by the electrical measurements resulted from uncertainties in the values of the constants of the electrical circuit. The resistances (R_1 and R_2 of fig. 11) were frequently measured. Since only the ratio of resistances was needed, the temperature of the resistance standards was not important as they had approximately the same temperature coefficients of resistance and were kept in the same oil bath. The load coefficients of resistance were important since the two resistance standards carried different loads, but these standards were designed to make the load coefficients very small. The error introduced by the use of the calibrated slide wire was always less than a part in a million. No effect of changing the grounding connection of the circuit could ever be detected. Thermal electromotive forces were always small and errors from this source were avoided by using a false galvanometer zero. Insulation resistance was found to be high throughout the circuit. The error in the ratio of the radii resulting from the electrical measurements was estimated to be less than three parts in a million.

15. RESULTS

The results of the measurements of the ratio of the radii can be conveniently shown in the form of tables. Table 8 gives typical detailed results with one set of coils (M2 S1) after all adjustments had been made, and shows how the actual data were taken and reduced. The close agreement of the individual measurements and the small deviations from the mean value show that the observational

[32] Unpublished communication. Method was developed by C. Huff.

errors with this apparatus were small. In fact, individual results were often carried to 1 part in 10 million to get significant differences.

TABLE 8.—*Ratio of radii:* M2:S1

[Typical set of data for the determination of the ratio of the radii]

Date 1932	Average slide wire reading [a]	Ratio of currents [b] I_2/I_1	Coil temperatures ° C		Corrections for temperature		Total correction [c]	Ratio of radii (a_2/a_1) at 22 C and no load [d]	Deviation from mean
			M2	S1	M2	S1			
May 13	833.8±0.5	3.4(1.002225)	23.84	21.58	-35×10^{-6}	-7×10^{-6}	$+20\times10^{-6}$	0.625(1.001427)	-2×10^{-6}
13	833.8±0.7	2225	.83	.58	−35	−7	+20	1427	−2
13	834.4±0.6	2224	.81	.57	−34	−7	+21	1427	−2
14	835.7±0.4	2221	.61	.59	−30	−7	+25	1428	−1
14	836.3±0.7	2220	.63	.58	−31	−7	+24	1426	−3
14	835.7±0.5	2221	.66	.57	−31	−7	+24	1427	−2
15	833.6±0.7	2224	.80	.60	−34	−7	+21	1427	−2
15	834.1±0.5	2224	.81	.60	−34	−7	+21	1427	−2
21	834.3±0.4	2220	.26	.62	−24	−6	+32	1434	+5
21	835.0±0.4	2218	.25	.68	−24	−5	+33	1433	+4
24	839.3±0.6	2208	22.63	.55	−12	−8	+42	1432	+3
24	839.1±0.6	2209	.65	.55	−12	−8	+42	1433	+4
Average of the 12 measurements								0.625(1.001429) / 0.6258931	$\pm3\times10^{-6}$

[a] The average of 10 observations. The slidewire, having a resistance of 7.6 ohms, was divided into 1,000 divisions and shunted across a resistance of 0.002097 ohm.

[b] The resistances used had the values 0.997090 ohm and 3.4 (1.001060) ohms with slight corrections for daily variations. The slidewire reading, divided by 1,000, gives the fraction of the 0.002097 ohm resistance to be added to the 0.997090 ohm resistance. This total is divided into the 3.4 (1.001060) ohms resistance to give the ratio of the currents.

[c] In addition to the temperature corrections, the total correction includes the following, in parts in a million: Load S1=−1; load M2=+4; leads =+1; length of magnet=+9; finite section of coils=+49.

[d] The ratio of the radii is obtained by multiplying the ratio of the currents by the ratio of the number of turns on the coils (72/392) and adding the total correction. The result is expressed as the product of the nominal ratio (0.625) times a number differing slightly from unity.

Table 9 gives all the results of the determinations of the ratio of the radii which were made on the eight combinations of coils. The 1911 values are given for comparison.

From the data given in table 9, four independent values of the ratio of the radii of the two moving coils have been computed. The average variation from the mean of these four values indicates the magnitude of the errors in the determinations. As shown in table 10, the average deviation from the mean is about three parts in a million. It can be shown that an error of three parts in a million in the ratio of the radii would have produced, in the most unfavorable case, an error of about

TABLE 9.—*Results of measurements of the ratio of the radii of the coils*

Coils	Ratio of radii of coils			Coils	Ratio of radii of coils		
	1911, corrected	1933, measured	1933, corrected [1]		1911, corrected	1933, measured	1933, corrected [1]
M2:L3	0.5001458	0.5001576	0.5001586	M2:S1		0.6258931	0.6258941
M2:L4	.5000498	.5000714	.5000701	M2:S2		.6261848	.6261844
M3:L3	.4013722	.4013764	.4013758	M3:S1	0.5022938	.5022786	.5022778
M3:L4	.4012952	.4013034	.4013045	M3:S2	.5025200	.5025107	.5025110

[1] The measured values were corrected to accord with the mean value of M2:M3 given in table 10.

four parts in a million in the absolute value of the current, which is much less than the observed inaccuracy. As the measurements of the ratio of the radii were sufficiently accurate for the purpose of this investigation, detailed data have been omitted.

In order to slightly improve the final result of this investigation, the mean ratio of the radii of the two moving coils (see table 10) was assumed to be correct, and the measured values of other ratios were corrected to make them consistent with this mean. These corrected values of the ratio of the radii are given in the last column of table 9, and are the ones used in the computations of the current in absolute measure.

TABLE 10.—*Computed ratio of the radii of the 2 moving coils using each fixed coil as intermediate*

Intermediate fixed coil	Ratio of radii M2:M3	Variation from mean
		Parts per million
S1	1.246107	−3
S2	1.246113	+2
L3	1.246107	−3
L4	1.246117	+6
Mean	1.246111	±3

VI. EXPERIMENTAL DETERMINATION OF THE MAXIMUM FORCE BETWEEN THE COILS

The experimental determination of the maximum force between the coils was accomplished by placing the two fixed coils in their correct positions and measuring the force at a number of positions of the moving coil. The fixed coils were placed by mechanical methods so that they were approximately coaxial and at the proper distance from each other. The axes of the coils were made vertical by leveling the coil forms. After making a set of measurements of the force, the fixed coils were sometimes readusted to reduce the corrections for maladjustment. Measurements of the force on the moving coil were made both with the currents in the two fixed coils in opposite directions and with them in the same direction. In the first case a large force was obtained (called the sum of the forces) and in the second case the resultant force was very small (called the difference of the forces). There would be no force in the second case if the two fixed coils were identical and the coils were in perfect adjustment.

1. MEASUREMENT OF THE FORCE FOR A GIVEN ARRANGEMENT OF THE COILS

For any given arrangement of the coils, the electromagnetic force produced by a current in the coils was compared with the gravitational force on a weight of known mass. A series of determinations of the rest point of the balance was made, but between each determination and the next the current in the fixed coils was reversed and at the same time the weight which counterbalanced the electromagnetic force was added or removed. The series of determinations of the rest point which is required for a measurement of the force is called a *run*. In

each run there were made at least 6 rest-point determinations, every one of which was obtained by reading at least 5 turning points of the optical lever attached to the balance beam.

To obtain the force for a given arrangement of coils, the rest points of a run were plotted as ordinates with the times of determinations as abscissas. Normally the plotted points lay on two parallel straight lines, one containing the points obtained when the direction of the current in the fixed coils was such that the weight was placed on the pan of the balance, the other when the current was reversed in the fixed coils and the weight removed. The change in the rest point,

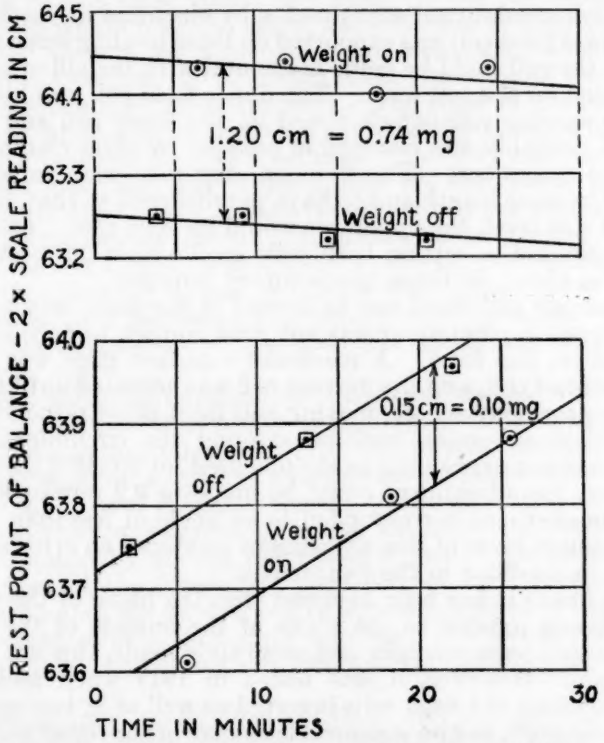

FIGURE 15.—*Data on typical runs with the current balance.*

The upper set, taken May 17, 1932, indicates that 0.74 mg should be added to the value of the weight (8.42986 g when corrected for the buoyancy of the air) to give the doubled electromagnetic force (8.43060 g) on the moving coil. The lower set, taken November 1, 1932, indicates that 0.10 mg should be subtracted from the value of the weight (11.91769 g when corrected for the buoyancy of the air) to give the doubled electromagnetic force (11.91759 g) on the moving coil. The above results are used in table 15.

obtained from the vertical distance between the two lines divided by the change in the rest point produced by one milligram, gave the difference between the electromagnetic force and the force produced by gravity on the mass of the weight which was added and removed from the pan of the balance during the determination. Figure 15 gives the plot of two typical runs.

In the normal case just described, the rate of change in the rest point during a run was generally constant (sometimes zero) as shown by the fact that the plotted points lay on straight lines. In some cases

the plotted points did not lie on straight lines. In general, the data obtained in such cases were discarded, but occasionally the points lay on smooth curves, having a constant vertical distance between them. The data obtained in such cases were used.

2. ADJUSTMENT OF THE COILS

It has been shown in section IV that there are 12 important adjustments to be made in placing the coils in the current balance, 6 of which are rotations of the coils and 6 translations. The correctness of the rotational adjustments was determined by means of levels; that of the translational adjustments by electrical methods.

The lower fixed coil was supported on three leveling screws by means of which the coil could be made horizontal with the aid of an accurate level placed on the coil form. The upper fixed coil was held in place by three spacing rods which rested on the lower coil and the whole fixed coil assembly was clamped in position by three clamping screws above the upper coil. The three spacing rods were carefully made to have the same length and to have parallel ends so that, if the lower fixed coil was level, the upper one would be level also. Little trouble was experienced in setting both coils level within 30 seconds of arc, which was about 10 times the accuracy required.

The moving coil could not be leveled in the same way as the fixed coils because the mounting was not rigid enough to permit a level to be placed on the form. A machinist's surface gage was placed on the lower fixed coil, and the moving coil was adjusted until the pointer from the gage touched the moving coil form at corresponding points when placed at several positions around the circumference. This method was not as accurate as the one used for leveling the fixed coils. With care, the adjustment could be made to 0.2 mm or less, which, for the smaller coil, corresponded to an angle of less than 5 minutes. The maximum error of this adjustment produced an error of less than one part in a million in the final result.

In the above it has been assumed that the plane of the winding of each coil was parallel to the plane of the outside of the coil form. Since the coils were carefully and accurately made, this is a reasonable assumption. However, it was tested in 1911 when measurements were made with the fixed coils inverted as well as in two orientations, differing by 120°, and no measurable change in the result was produced by either change. These tests were not repeated in this investigation, since the same coils were used.

The translational adjustments are most easily described by referring them to a system of rectangular coordinates, having the origin midway between the planes of the fixed coils and midway between their vertical axes, and having one coordinate axis vertical, one north and south and the third east and west. The description is also simplified by assuming that the two fixed coils of each combination are exactly alike. The coils used are so nearly alike that this does not affect the conclusions. The moving coil was moved in the direction of each of the coordinate axes, and the sum of the forces for a given current was observed at several positions. For the adjustment along the vertical axis, the force was a maximum when the moving coil was midway between the two fixed coils. For the adjustment along either of the

horizontal axes, the force was a minimum when the center of the moving coil coincided with the other horizontal axis. If the two fixed coils were so perfectly adjusted that their axes coincided and that they were at the correct distance apart for both coils to produce maximum force on the moving coil when placed midway between them, then the sum of the forces, when the center of the moving coil was at the origin of coordinates, would be the force required for the computation of the absolute value of the current.

The correction for the imperfect adjustment of the fixed coils was obtained by measuring the difference of the forces at several points along each of the three coordinate axes. If the adjustments were perfect, at all points near the origin the difference of the forces would be the same (zero if the fixed coils were identical). If the adjustments were not perfect, the difference of the forces would vary linearly with the displacement along the axes. The slope of the line for the difference of forces along the vertical axis could be changed by varying the distance between the two fixed coils. In every case the distance between the fixed coils was changed until the line had so little slope that the correction for lack of correct spacing was less than a part in a million. In the case of the two horizontal axes no attempt was made to adjust the fixed coils so that they would be more nearly coaxial, but the correction for lack of coaxiality was seldom more than one or two parts in a million. The theory by which the correction for imperfect adjustment of the coils was made has been given in section IV.

An actual series of adjustments was made as follows: The coils were leveled and placed as nearly as possible in their correct position by mechanical measurements. With the current through the coils maintained constant, a series of measurements of the sum of the forces was made for several different vertical positions of the moving coil. The vertical position was read by noting the rest point of the balance, and was changed by adding weights to a pan of the balance. The observed sum of the forces was then plotted as ordinate with the vertical position of the moving coil as abscissa, a series of observations giving a curve with a maximum ordinate. At the position of the maximum force, the moving coil was midway between the two fixed coils.

With the current maintained constant and the moving coil kept midway between the two fixed coils, the sum of the forces was measured for several positions of the moving coil along one horizontal axis (say the north-south direction). This adjustment was made by a displacement of the entire balance as described in section II and the position was measured in terms of the revolution of the screw by which the adjustment was made. The sum of the forces was plotted as ordinate and the position in the north and south direction as abscissa, a set of observations giving a curve with a minimum value of the sum of the forces at a definite north and south position. The moving coil was placed at the position indicated by the minimum point and an exactly similar adjustment made in the east-west direction. When the moving coil was placed at the minimum position in the east-west direction, the center was then midway between the axes of the two fixed coils and midway between their planes, i.e., at the origin of coordinates.

3. SUM OF THE FORCES

Following the adjustments outlined above, a set of measurements of the sum of the forces was made, to be used in determining the force from which the absolute value of the ampere could be computed. The set consisted in measuring the force with the center of the moving coil as near as possible to the origin of coordinates, then at two positions equally displaced from the origin, and located on the same coordinate axis, then again at the origin, followed by two positions equally displaced along another coordinate axis, etc. A complete set consisted of at least 4 measurements at the origin, and, for each of the coordinate axes, 2 measurements at points equally displaced from the origin. The horizontal position was relatively stable so that two measurements equally displaced from the origin were a sufficient check on each horizontal adjustment. The vertical position of the moving coil and also the optical system by which its position was measured depended on several variable factors so that the vertical adjustment was checked often, usually daily.

Each series of measurements made at a given position of the moving coil has been defined as a *run*. If the center of the moving coil is at the origin of coordinates, the run is called a *final run*. At other positions of the moving coil, the runs are called *adjustment runs*.

All of the final runs in each set of measurements were included in determining the value of the ampere. The adjustment runs served merely to insure that the center of the moving coil was at the origin of coordinates during the final runs. Since the shape of the curve connecting force and displacement was known from the preliminary set of measurements, three points were enough to determine the whole curve. The value of the electromagnetic force between the coils after all the adjustments had been made was thus determined from each of the final runs, and this value was used in computing the value of the current in absolute measure. The results are given in a following section.

4. DIFFERENCE OF THE FORCES

The principal reason for measuring the difference of the forces was to correct the sum of the forces for the lack of coaxiality of the fixed coils and for their incorrect spacing. In the region near the origin of coordinates, the difference of the forces is a linear function of the displacement of the moving coil along any coordinate axis. For obtaining the correction to the sum of the forces, only the slope of the line obtained by plotting the difference of forces against displacement of the moving coil is required. Hence for this purpose, measurements were necessary only at two positions along each coordinate axis, but, as a check, were made at three or more positions.

Additional reasons for measuring the differences of the forces were to obtain a check on the computations and to determine the effect of the magnetic properties of the surrounding medium on the measured sum of the forces. The latter reason will be considered in another section. In computing the force for unit current, the computations were made separately for each pair of coils. By subtracting the values, the computed difference of the forces for unit current was obtained. The difference of the forces was then measured with a

known current in the coils and the result compared with the computed difference for this current. Since the computed difference is the result of the subtraction of two large and nearly equal quantities, a small error in measuring the ratio of the radii of the coils, or in computing the maximum force for either coil, or in adjusting the coils will produce a relatively large difference between the observed and computed difference of the forces.

The results obtained on the difference of the forces are given in the next section. They were subject to two possible errors, which were peculiar to these measurements only. The lead correction was made only for measurements of the sum of the forces. Since the connections were slightly different when the difference of the forces was measured, the lead effect might have been slightly different in the two cases (sum and difference of the forces). This was not realized at the time the measurements were made but as it could not affect the absolute value of the current, the measurements were not repeated.

In 1911 it was found that the value of the difference of the forces changed slightly when the two fixed coils were interchanged, the mean of the two values differing less from the calculated values than either value alone. The effect was small and did not seem important enough to justify the extra work which would have been required to investigate this point.

5. SOURCES OF ERROR AND CORRECTIONS

There are several sources of error in the absolute measurement of the current by means of the current balance. Corrections could be made for most of them, and those for which no correction could be made were thought to be small. Many of them are the same as those already discussed in connection with the measurement of the ratio of the radii. Some of these were of such a nature that they tended to cancel errors made in the measurement of the ratio of the radii, while others were independent of the previous measurements. The major sources of error and the corrections to be made for them will be considered in the following paragraphs.

(a) ADJUSTMENT OF THE COILS

Since there were 12 adjustments which were independent, one might expect that the total error would be relatively large. However, at various times, the coils were removed, replaced, and readjusted, and whenever this was done, the results of the measured force in the two cases agreed within a few parts in a million. It is estimated that the error caused by maladjustment of the coils never exceeded six parts in a million in the determination of the force or three parts in a million in the measurement of the current.

(b) SENSITIVITY OF THE BALANCE

The sensitivity of the balance was used in determining the small difference between the force of gravity on the weight and the electromagnetic force between the coils. In practice the weights and resistances used with a particular set of coils were adjusted so that the difference between the gravitational and electromagnetic forces was very small, in which case the sensitivity of the balance did not need

to be known accurately. Nevertheless, the sensitivity was measured frequently and found to change very little after the balance and coils were set up and adjusted. It is estimated that the error in the measured sensitivity did not produce an error in the measured force as large as one part in a million.

(c) WEIGHTS AND BUOYANCY CORRECTION

The masses of the weights were measured by the mass section of this Bureau and the results certified to be correct to 0.01 mg. They were measured before and after each complete series of force determinations and the change in mass of any weight was never larger than 0.01 mg.

The density of the gold-platinum weights was 19.5 and of the platinum-iridium weights was 21.5 grams per cubic centimeter. The correction to the force for the buoyancy of the air at a temperature of 22 C, a pressure of 760 mm, and a relative humidity of 50 percent, was 63 parts in a million for the gold-platinum weights and 57 parts in a million for the platinum-iridium weights. The high density of the weights not only decreased the correction for buoyancy of the air, but minimized the changes in the buoyancy correction caused by changes in the temperature, pressure, and humidity of the air. The temperature, pressure, and humidity of the air were always measured, and the standard buoyancy correction modified, if necessary. The error introduced into the measurement of force by errors in the determination of the mass of the weights and in the buoyancy correction was estimated to be less than two parts in a million, which would make an error of less than one part in a million in the value of the current.

(d) ACCELERATION OF GRAVITY

The value of the acceleration of gravity was as important a factor as the mass in determining the gravitational force. The value of gravity which has been used in this investigation depended directly on the determination of the absolute value made in Potsdam,[33] Germany, where a value of 981.274 $\pm$0.003 cm/sec^2 was obtained. The value at a base station in Washington has on three occasions been accurately compared with that at Potsdam by means of pendulums, once [34] in 1900, a second time [35] in 1928–29, and again [36] in 1933. The value of gravity at the present base station in the Commerce Building,[37] in Washington, resulting from each of these determinations is as follows:

1900	980. 113 cm/sec^2
1929	980. 118
1933	980. 118

The transfer in Washington from the Coast and Geodetic base stations to the Bureau of Standards was made in 1910 and in 1933. The determination made in 1910 at this Bureau gave a value of

[33] Veroeffentlichung des Konigl. Preus. Geodätische Institutes, Neue Folge no. 27, 1906.
[34] U.S. Coast and Geodetic Survey Report for 1901, appendix 5.
[35] A determination of the relative value of gravity at Potsdam, Greenwich, Ottawa, and Washington, by A. H. Miller. Pub. of the Dominion Observatory, Ottawa, vol. 11, no. 2, 1931.
[36] The report on this comparison has not yet been published, but the result has been communicated by letter to the authors.
[37] The values here given for 1900 and 1929 are 0.001 cm/sec^2 higher than values published when the determinations were made, since those applied to the former Coast and Geodetic base station which is now abandoned.

980.095 cm/sec^2 for the acceleration of gravity at a pier in the basement of the south building. This value was based on the transfer made in 1900 from Potsdam. The measurements made in 1933, following the 1933 transfer from Potsdam, gave a value of 980.100 cm/sec^2 at a pier in the constant temperature room of the east building, which pier is 6.4 meters below the level of the old pier. Correcting for this difference in level, the 1933 value at the level of the old pier is 980.099 cm/sec^2.

The value assigned to the acceleration of gravity at this Bureau depends not only on the transfer from Potsdam to the Washington base station but also on the transfer from the Washington base station to the Bureau. Since in neither case do the 1933 values agree with the older values, four possible values may be assigned to the acceleration of gravity at any place at this Bureau. The four values at the elevation of the current balance (103 meters above sea level which is also the level of the old pier) are:

Washington base station to Bureau	Potsdam to Washington	
	1933	1900
1910	980.100 cm/sec^2	980.095 cm/sec
1933	980.099	980.094
Mean	980.100 cm/sec	980.095 cm/sec^2

An absolute determination of the value of the acceleration of gravity is now in progress at this Bureau, but the result is not yet available. There are, however, indications that the value obtained from this determination may differ by several parts in a million from the value as transferred from Potsdam. Hence, pending a decision as to the most probable value at this Bureau, the value used in 1911 has been retained in this investigation, making a correction for the difference in elevation of the two laboratories. The value which has been used is 980.095 cm/sec^2. Had the result of the recent transfer from Potsdam been used, the final value of the current would have been changed by only two parts in a million, which is negligible in comparison with other errors.

(c) CORRECTION FOR THE TEMPERATURE OF THE COILS

To correct the measured force for the change in radius produced by the difference between the temperature of the coils and the standard temperature (22 C), the change in the radius of each coil produced by this temperature difference was computed from the temperature coefficient of expansion. If a is the radius of a coil, τ its coefficient of expansion, and Δt the amount by which the measured temperature exceeds the standard temperature, then from equation 43 the increase in its radius, Δa is given by the equation

$$\Delta a = a\tau\Delta t \quad \text{or} \quad \Delta a/a = \tau\Delta t. \tag{51}$$

It follows that the relative change in the ratio of the radii, $\Delta\alpha/\alpha$, of the two coils having, at the standard temperature, radii a_1 and a_2, respectively, is

$$\Delta\alpha/\alpha = \Delta a_2/a_2 - \Delta a_1/a_1 = \tau_2\Delta t_2 - \tau_1\Delta t_1 \tag{52}$$

where all symbols having a subscript two apply to the small coil, and those having subscript one to the large coil.

The relative change in the maximum force corresponding to a known relative change in the ratio of the radii is given by the formula (see equation 5)

$$\frac{\Delta \mathfrak{F}_m}{\mathfrak{F}_m} = \epsilon \frac{\Delta \alpha}{\alpha} \tag{53}$$

where $\mathfrak{F}_m$ is the maximum force, α the ratio of radii and ϵ is a constant for any particular value of the ratio of the radii. The value of ϵ can be computed from the ratio of the radii by the formula [38]

$$\epsilon = \frac{\beta}{2x^2} = \frac{1-\alpha^2}{2y_m^2} = \frac{(1-\alpha^2)}{2\left(\frac{1}{2} - \frac{9}{20}\alpha^2 - \frac{1}{16}\alpha^4\right)^2} \tag{54}$$

where y^m is the ratio of the distance for maximum force to the radius a_1 of the large coil. A table of the values of ϵ for different values of α from 0 to 1 had been prepared by Grover [39] before the development of the above formula. The values which were used in the present investigation were computed from equation 54 and are given in the following table.

TABLE 11.—*Values of the constant* ϵ *used in the equation*

$$\frac{\Delta \mathfrak{F}_m}{\mathfrak{F}_m} = \epsilon \frac{\Delta \alpha}{\alpha}$$

α	ϵ
0.4013	2.312
.5001	2.549
.5023	2.555
.6260	3.083

From equations 52 and 53 the expression for determining the maximum force at the standard temperature, $(\mathfrak{F}_m)_{22}$, from the force at the observed temperature, $(\mathfrak{F}_m)_{obs}$ is

$$(\mathfrak{F}_m)_{22} = (\mathfrak{F}_m)_{obs}\,[1 - \epsilon(\tau_2 \Delta t_2 - \tau_1 \Delta t_1)]. \tag{55}$$

The errors made in applying the temperature correction of the coils were the same as those in the determination of the ratio of the radii which have already been discussed. It is to be noted, however, that if the temperatures of the coils in the measurement of the ratio of the radii were the same as when the coils were used in the current balance, the correction to standard temperature would be the same in both cases, so that no error would result. In practice it was not possible to have the two temperatures the same, but efforts were made to keep them as close as possible. No error was caused by assuming that the value of the temperature coefficient of resistance of the copper wire in the coils was 0.0039 per degree centigrade since this value was used in the measurement of the coefficient of expansion as well as in

[38] This formula is adapted from equation 23 of Snow's paper. See footnote 25 for reference.
[39] Table 5, p. 373 of Grover's paper. Reference footnote 15.

its application. It is estimated that the total error introduced into the final value of the current because of errors in the temperature correction was not more than two parts in a million.

(f) CORRECTION FOR THE ELECTRICAL LOAD ON THE COILS

In order to correct the observed force for the electrical load on the coils a formula for the load correction was derived from equations 43 and 53 in the same manner as equation 55 for the temperature correction. The formula is

$$(\mathfrak{F}_m)_0 = (\mathfrak{F}_m)_{obs}[1 + \epsilon(\psi_2 p_2 - \psi_1 p_1)] \tag{56}$$

where

$(\mathfrak{F}_m)_0$ = the maximum force per unit current that would have been obtained with two coils if their loads had been zero
$(\mathfrak{F}_m)_{obs}$ = the force per unit current with the observed load
ψ_1 and ψ_2 = the load coefficients of the large coil and the small coil respectively
p_1 and p_2 = the loads in watts.

The value of ϵ is the same as given in equation 54.

One of the best checks on the accuracy of the load corrections was the good agreement obtained between the results taken with different currents and hence different loads. The error that may have been introduced into the final value of the current because of errors in the load correction is estimated to be less than three parts in a million.

(g) LEAD CORRECTION

The correction for the leads to each of the coils of the balance was determined experimentally. The terminals of each winding of each coil were constructed so that the windings could be disconnected by melting drops of solder and the leads short-circuited by adding a drop of solder. (See fig. 3, p. 672.) When this was done for the fixed coils alone, an experimental determination of the force with normal current through the moving coil and the fixed-coil leads gave the correction for the fixed-coil leads. The correction for the moving-coil leads was determined in a similar manner. The algebraic sum of the two gave the total correction, which was seldom more than a few parts in a million. This was determined for every coil combination. The error in this measurement was about the same as in any force determination, producing an error on the final result of not more than two parts in a million.

(h) CHANGES IN THE REST POINT DURING A RUN

During an actual run, there were often slight irregularities superimposed upon the uniform rate of change of the rest point. (See fig. 15.) In such a case, the number of rest-point determinations was increased. The number of observations required for a run was determined by the operator. As the data were taken, the observer judged whether the points would lie on two parallel straight lines. If the first six points appeared to satisfy the above condition, the operator decided that sufficient observations had been made for a run. If the first six points did not appear to be satisfactory, several more were taken until it appeared certain that there were enough points to

establish a satisfactory average line. Under normal conditions, an experienced operator could repeat results by this method to within 0.02 mg. When the total electromagnetic force was 10 grams, the maximum error from this source was two parts in a million in the determination of the force, causing an error in the measurement of the current of one part in a million. When the force was smaller, that is, when smaller currents were used, the relative error was larger.

(i) CONVECTION CURRENTS IN THE AIR

Air currents which affected the balance were set up around both the moving coil and its flexible leads by the heat produced by the current in them. These air currents caused, on the parts with which they were associated, an upward force, equivalent to a few tenths of a milligram. However, the method of comparing the electromagnetic and gravitational forces, by reversing the current in the fixed coils and at the same time adding or removing a weight, allowed the heating of all parts to remain constant and therefore the air currents should have remained constant. However, these air currents were very susceptible to changes in the temperature of surrounding objects. The effect of any change in the air currents was to alter the rest point of the balance. Methods of minimizing the effect of slight irregularities in the rest point have already been discussed and the error produced by such irregularities has been estimated in the preceding paragraph.

(j) MAGNETIC BODIES

Magnetic bodies may, in considering their effect on the measured force, be divided into the three following classes:

(1) *Magnetic masses attached to the moving system.*—The magnetic masses which were attached to the moving system produced a force by virtue of the attraction between them and the fixed coils. If this force had been appreciable, the rest point of the balance would have changed when the current in the fixed coils only was changed from zero to its normal value. No definite effect was ever found. The only magnetic masses in the moving system were the steel knife edges of the balance beam and they were located a little more than a meter from the nearest coil. The magnetic field of the moving coil would tend to magnetize the moving masses, so that all material in the moving system that was near the coil was carefully tested and was found to be nonmagnetic.

(2) *Magnetic masses outside the balance.*—The magnetic masses which were outside the balance produced a force because of the attraction between them and the moving coil, and also a possible attraction between them and the moving magnetic masses on the balance. However, in these measurements, the field of the fixed coils was reversed so that only that portion of the attraction which reversed when the field of the fixed coils reversed caused an extraneous force that was included in the measured force. Permanent magnets produced no error because the sign of the force caused by them did not change when the field of the fixed coils was reversed. However, soft-iron masses which were magnetized by the field of the fixed coils reversed the sign of their force on the moving coil when the magnetizing field of the fixed coils was reversed, and if unsymmetrical with respect to the coils, would affect the measured force. Unsymmetrical

soft-iron masses generally produced a greater error in measuring the difference of the forces than in measuring their sum, since the external magnetic field above and below the coils was greater in the former case. The agreement between the computed and observed difference of the forces indicated that the presence of existing unsymmetrical soft-iron masses (if any were present) had little effect on the difference of the forces. If the fixed masses were symmetrical, the measurement of the difference of forces would not have detected them.

The only iron masses which were approximately symmetrical were the pipes in a shaft at a distance of about 3 meters from the balance. These were so distant that no effect appeared probable.

In addition to the iron pipes, there was some iron machinery about 3 meters above the balance. In 1911 it was found that 75 kg of iron placed 116 cm below the moving coil had an effect of not more than one part in a million on the sum of the forces and about 10 times as large an effect on the difference of the forces. The effect of a given mass of iron decreased rapidly with increase in distance. Since there was no appreciable amount of iron within 3 meters of the balance, the error caused by fixed magnetic masses must have been much less than a part in a million. The measurements on the difference of the forces support this conclusion.

The water jacket of brass or copper which surrounded the moving coil was so close to the coil that a slight magnetic susceptibility might affect the force on the moving coil. The jackets were tested for their magnetic properties with the astatic magnetometer (see p. 710) and their susceptibilities were found to be essentially unity. In addition, weighings with and without the jackets gave no difference in the results.

(3) *Magnetic bodies as a part of the coils themselves.*—Magnetic bodies which were a part of the coils themselves might have caused the external fields to be different from those computed, and therefore have caused the measured force to be different from the computed force. This was tested in 1911 by sticking iron filings to a piece of cloth and wrapping it around the fixed coils. No effect was noted. Also, the two sets of large fixed coils L1 L2 and L3 L4 used in 1911 differed principally in their magnetic properties. When brought in turn near an astatic magnetometer, coils L1 and L2 produced a deflection of the needle about 100 times that produced by L3 and L4. The absolute value of the current obtained with the two sets of coils agreed closely. These two lines of evidence indicate that the magnetic properties of the particular coils used in this work had a negligible effect on the force.

(k) EXTERNAL MAGNETIC FIELDS

The effect of the external magnetic field was measured by observing the change of force when the current through the moving coil was reversed; there being no current in the fixed coils. On several occasions the change of force was about 0.7 mg when a current of 0.8 ampere in the moving coil was reversed. This force, when constant, produced no error in the comparison of the electromagnetic and gravitational forces, because the moving-coil current was not reversed during a measurement. The only chance for error was in case the external nonuniform magnetic field changed during a run. Such a change would cause an irregularity in the rest point which could not

be distinguished from irregularitites caused by variations in the convection currents in the air. The graphical method of treating the rest-point data gave an opportunity for eliminating such an irregularity. In plotting the curve connecting the rest point with the time of observation, a single point, which did not lie on the curve through the remaining points, could be neglected on the assumption that the rest point had been displaced by a change in the nonuniform portion of the external magnetic field. The ease with which such unusual points were detected and eliminated was an added reason for using the graphical method for the treatment of the observed data. (See fig. 15.)

(l) CORRECTION FOR THE FINITE CROSS SECTION OF THE COILS

The errors which arose in applying the correction for the finite cross section of the coils were caused by the uncertainty in the actual cross sections. A formula[40] for the effect on the force of estimated errors in the cross-sectional dimensions has been obtained by adding the derivatives of the expressions for the effect of cross section on the ratio of the radii (equation 49) and on the force between the coils (equation 7). The formula is

$$\frac{\delta\mathfrak{F}_m}{\mathfrak{F}_m}=\frac{1}{2x^2}\left\{\left[\frac{(1+\beta)\lambda_2}{3}-\beta\right]\left[\frac{c_1^2}{a_1^2}\frac{\delta c_1}{c_1}-\frac{b_1^2}{a_1^2}\frac{\delta b_1}{b_1}\right]\right.$$
$$\left.+\left[\frac{(1-\beta)\lambda_2}{3}+\beta\right]\left[\frac{c_2^2}{a_2^2}\frac{\delta c_2}{c_2}-\frac{b_2^2}{a_2^2}\frac{\delta b_2}{b_2}\right]\right\} \qquad (57)$$

The symbols have the same significance as in equation 7 p. 684. For a coil with square cross section ($b=c$) the error in the force for a given error in b is the same, but of opposite sign, as for a like error in c.

The errors, computed by the above formula for $\delta_b=\delta_c=+0.0005$ cm (each dimension in error by $+0.01$ mm), are given in table 12 for each pair of coils that was used. They are in substantial agreement with those obtained in 1911 by a different procedure.[41]

TABLE 12.—*Effect of errors in the sectional dimensions of the coils on the computed value of the force per unit current.*

Radii		Dimensions of square section		$\delta\mathfrak{F}_m/\mathfrak{F}_m$—parts per million for $\delta b=\delta c=+0.0005$ cm	
Fixed a_1	Moving a_2	Fixed $2b_1=2c_1$	Moving $2b_2=2c_2$	Fixed coil *	Moving coil *
cm	*cm*	*cm*	*cm*		
20	10	1.58	1.0	±0.59	±8.33
25	12.5	2.00	1.0	±.47	±5.33
25	10	2.00	1.0	±.29	±6.64
20	12.5	1.58	1.0	±1.20	±7.61

* The error is positive for the radial dimensions (c) and negative for the axial dimensions (b).

The errors are independent, that is, they may have either sign, so that the actual error caused by all errors in the sectional dimensions is not equal to the resultant of the separate errors.

[40] Equation 27 of Snow's paper. Reference footnote 25. The term $\delta r/r$ of Snow's equation has been assumed to be zero.

[41] See table XIII on p. 334 of reference in footnote 8.

The importance of accurately knowing the sectional dimensions is evident from the table. Also, the dimensions of the moving coils are more important than those of the fixed coils. From an analysis of the data which were obtained when the coils were wound, the authors have concluded that each dimension of each coil may have been in error by as much as 0.02 mm. Hence the maximum possible error, in $\mathfrak{F}_m$, even with the pair of coils in which a knowledge of the sectional dimension was most important, was only 36 parts in a million, corresponding to an error of 18 parts in a million in a determination of the current.

(m) ERRORS RESULTING FROM DIFFERENCES BETWEEN THE ACTUAL AND THE THEORETICAL COILS

The actual coils differed somewhat from those which were assumed in developing the theory of the current balance. The conditions that the actual coils failed to meet were (1) the wires were not uniformly distributed throughout the cross sections of the coils; (2) the currents in the two windings of a coil when connected in parallel were not exactly the same; (3) the distribution of the current in the cross section of any wire may not have been uniform, and (4) the coils were not exactly circular. No estimate has been made of the error introduced by the first of these conditions. The second has been tested experimentally and the third and fourth have been treated theoretically.

The theory of the current balance has been developed on the assumption that the wires of each layer are uniformly spaced and that the wires of different layers all lie in planes which are perpendicular to the axis of the coil. Such a condition cannot be met in any actual coil, and in coils with a double winding, such as used in this investigation, the deviation from the theoretical condition was necessarily appreciable. The wires of each layer were wound in spirals, and because of slight irregularities in the wires were never perfectly spaced. But perhaps the greatest difficulty arose in transferring the wires from one layer to the next. According to theory the wires should be transferred from one layer to the next on a radius of the coil. In the actual coils a small fraction of a turn was required for this transfer. No satisfactory method for estimating the effect of these imperfections on the final result has been developed.

Each coil had two windings which were placed side by side as the coil was wound. In using the coil these two windings were connected in parallel. As the resistance of the two differed slightly, one winding carried more current than the other. The current could be made the same in the two windings by adding a small resistance in series with the winding having the lower resistance. The effect on the force of equalizing the currents in the two windings was too small to be detected experimentally.

The effect of a nonuniform current distribution in each wire has been investigated theoretically.[42] It was shown that the distribution produced no effect on the absolute value of the current provided the ratio of the radii was measured by the electromagnetic method.

The effect of the lack of circularity of the coils on the force can be estimated by computing the force that would have been exerted if each coil had been composed of two semicircles, one having a radius

[42] See conclusion of Snow's paper. Reference footnote 25.

equal to the largest radius of the actual coil and the other having a radius equal to the smallest radius of the coil. Such a computation has been made for the coils L3 and M2, which were the two that showed the greatest departure from circularity when measured during construction. The correction to the force as computed for a circular coil was less than a part in a million.

(n) PREDICTED ERROR IN THE ABSOLUTE VALUE OF THE CURRENT

The maximum error in a single determination of the absolute value of the current could be predicted by summing the estimated errors for the different effects that have just been described. For convenience, the estimated errors will be divided into two classes, (1) those which are apparent from measurements on a single set of coils and (2) those which are disclosed only when the results on two or more sets of coils are available. Summing the estimated errors of the first class, no result of the absolute value of the current should differ from the mean obtained with that set of coils by more than 10 parts in a million. The results given later show that so large a deviation was seldom encountered. Hence it is probable that all the important sources of error which are disclosed by measurements with a single set of coils have been considered.

In the preceding discussion, an estimate has been made of the maximum possible effect on the absolute value of the current of three errors, the influence of which, on the absolute value of the current, can only be detected by measurements with different combinations of coils. These errors are those affecting the ratio of the radii, the adjustment of the coils in the current balance, and the cross-sectional dimensions of the coils. The maximum possible difference from the mean of the average result on any set of coils was estimated from these 3 errors to be 24 parts in a million in the absolute value of the current. This maximum possible difference is much less for 1 combination of coils than the observed difference from the weighted mean result, is very nearly equal for 2 combinations of coils, and is much greater for only 1 combination of coils. (See table 16.) Of the 3 errors which might cause this difference, the first 2 were checked experimentally, and the errors found to be approximately those estimated. Those concerning the cross-sectional dimensions of a coil can be checked by assuming an error in the dimensions of a coil that will make the result for a coil combination in which it was used the same as the mean result of all the coils. No reasonable assumption concerning cross-sectional errors will provide corrections that will give the same absolute value of the current for each set of coils. Hence there appears to be some source of error for which no estimate has been made, perhaps some of those discussed in (m).

VII. THE VALUE OF A CURRENT IN B.S. INTERNATIONAL AMPERES AND IN ABSOLUTE AMPERES

The value, in absolute amperes, of one B.S. international ampere, has been obtained from observations on four combinations of coils. For each coil combination, a number of sets of observations were made

and the results averaged to obtain a value for that combination of coils. The final value is the weighted average of the results for the four combinations of coils.

The first step in determining the absolute value of the current from the measured force was to compute the constant $\mathfrak{F}_m$ for each pair of coils. This was done by the methods given in section IV using the corrected values of the ratio of radii as given in table 9. The results of the computation are given in table 13.

TABLE 13.—*Constants for computing the current from the force*

[For nomenclature see equation 7,[a] p. 684]

Coils	Ratio of radii	y_m	F_m	Δ_2	Δ_4	$\mathfrak{F}_m$	Increase from 1911 value[b]
							Parts per million
M2:L3	0.5001586	0.3835	5.356342	-88×10^{-6}	$+0.5\times10^{-6}$	5.355877	−6
M2:L4	.5000701	.3836	5.353925	−110	+.3	5.353340	−2
M3:L3	.4013758	.4259	3.146497	+413	+.6	3.147797	−2
M3:L4	.4013045	.4259	3.145207	+395	+.5	3.146452	0
M2:S1	.6258941	.3141	9.98532	−225	+8.1	9.98315	
M2:S2	.6261844	.3139	9.99959	−241	+8.0	9.99726	
M3:S1	.5022778	.3825	5.414473	+404	+1.0	5.416654	−1
M3:S2	.5025110	.3823	5.420902	+393	+1.9	5.423043	+2

[a] The term $\frac{(x\Delta_2')^2}{2\lambda_2}$ in equation 7 was computed and found to be less than 0.3×10^{-6} for each combination of these coils.

[b] The 1911 values were corrected, by equation 53, for the observed change in the ratio of the radii.

The results of all the final runs taken with the four sets of coils are given in table 14 for the difference of the forces and in table 15 for the sum of the forces. There are given in those tables the corrections that were computed from the data, and, for each set of observations, the result that was obtained. The sum of the forces is used to compute the absolute value of the current while the difference of the forces is used merely as a check on the other work as a basis for making small corrections and as a guide in weighing results.

In table 14 is given a summary of the results on the differences of the forces. It is self-explanatory except for the last column in which is listed the indicated error that would be introduced into the absolute value of the current if the computed difference in forces minus the observed difference was all caused by an error in the computed value of one of the forces. As the value for each coil combination has been computed at least twice by different computers, the indicated error is not the result of a numerical mistake. As it is appreciably larger for the coil combination S1 S2 M2 than for any of the others, the absolute value of the current obtained with that coil combination is probably less reliable than the values obtained with the other combinations. For this reason the indicated error has been used as a guide in weighting the results on the absolute value of the current as obtained with different coil combinations.

TABLE 14.—*The difference of the forces*

Date	Coils	Nominal ratio of radii	Current	Computed difference	Number of observations	Average observed difference	Average deviation between observed values	Computed minus observed values	Indicated error in final value of current
			Amperes	*Milligrams*		*Milligrams*	*Milligrams*	*Milligrams*	*Parts per million*
1932	L3 L4 M3	0.4	1.018	1.80	5	1.67	0.02	+0.13	7
1932	do	.4	0.678	0.80	2	0.82	.00	−.02	2
1930	S1 S2 M3	.5	.679	2.30	6	2.26	.03	+.04	4
1931	L3 L4 M2	.5	1.018	2.50	3	2.43	.04	+.07	4
1927	do	.5	0.768	1.42	3	1.36	.01	+.06	6
1931	do	.5	.678	1.11	4	1.10	.01	+.01	1
1931	do	.5	.509	0.63	1	0.64		−.01	2
1932	S1 S2 M2	.626	1.018	8.42	3	8.92	.01	−.50	25
1932	do	.626	0.678	3.74	3	3.92	.02	−.18	18

In table 15 are given the essential data for all final runs for determining the value of the current in absolute amperes from the sum of the forces, and the relation between that value and the value of the current in international amperes. In the first three numbered columns are given the coil combination and the temperatures of the moving coil and of the fixed coils. In the case of the fixed coils the average temperature of the two coils is given, there being seldom any significant difference between them. The temperatures of the coils were always determined immediately after the measurement of the sum of the forces by measuring the resistance of the windings with the same current in them as was used in measuring the force. The temperature of the moving coil depended somewhat upon the type and position of the water jacket, but the results were independent of the water jacket so that no detailed discussion has been given.

In the fourth column is given the observed doubled force in grams, which resulted from the reversal of the current. The difference in the rest points when the current was reversed (at the same time that the weight was added or removed) was multiplied by the sensitivity of the balance to obtain the amount that should be added to, or subtracted from, the value of the actual weight in order that the electromagnetic and gravitational forces should be equal. (See fig. 15, p. 713.) The gravitational force on the weight was corrected for the buoyancy of the air.

In the fifth column is given the correction to the observed doubled force for the temperature of the coils. A standard temperature of 22 C was chosen to conform with the work in 1911.

In the sixth column of the table is given the sum of the corrections for the loads on the coils and for the leads to the coils. For a given set of coils carrying a given current, the load correction was a constant and the lead correction had a definite value so long as the position of the leads was not changed. The latter was determined experimentally whenever a set of coils was installed in the balance.

In the seventh column is given the corrected doubled force corresponding to 22 C and no load which is obtained by adding, for each row, the values in columns 5 and 6 to the observed doubled force.

The eighth column contains the absolute value of the current as computed from the doubled force (column 7) and the dimensions of the coils. To compute the current, the force of gravity on the weights is equated to the electromagnetic force between the coils, giving the formula

$$2\,M\,g = 2\,n_1 n_2\,(I_a/10)^2\,(\mathfrak{F}_1 + \mathfrak{F}_2) \tag{58}$$

where

$2\,M$ = observed doubled force in grams corrected to 22 C and no load

g = acceleration of gravity in cm/sec^2

$2\,M\,g$ = observed doubled force in dynes corrected to 22 C and no load

n_1 = number of turns of wire on each of the fixed coils

n_2 = number of turns of wire on the moving coil

I_a = current in absolute amperes (1 absolute ampere = $\frac{1}{10}$ cgs electromagnetic unit of current)

$\mathfrak{F}_1$ = computed constant for the moving coil and one of the fixed coils at 22 C including corrections for the cross sections of the coils

$\mathfrak{F}_2$ = computed constant for the moving coil and the other fixed coil

Solving for the current

$$I_a = \frac{10\sqrt{2\,M\,g}}{\sqrt{2\,n_1 n_2\,(\mathfrak{F}_1 + \mathfrak{F}_2)}} \tag{59}$$

In the ninth column is given the value of the same current in B.S. international amperes. This was obtained by dividing the numerical value of the potential difference which the current produced at the terminals of a standard resistor by the numerical value of the resistance, both electrical quantities being measured in terms of the units as maintained [43] by the Bureau of Standards.

In the tenth column are listed the differences between the value of the current in B.S. international amperes and in absolute amperes, divided by the value of the current in absolute amperes. These relative differences are related to the ratio of the two units as experimentally determined for each current and hence should all have the same value regardless of the particular value of the current used and of the external conditions of measurement. These numbers have been averaged by groups to obtain the final result of this investigation.

In the eleventh and last column is given the difference between each number in the tenth column and the mean value of the particular group to which it belongs. The numbers of this column indicate the uniformity of the experimental values with a given set of coils.

[43] The values given in this paper are based on the units of resistance and electromotive force as maintained at the time the individual measurements were made. On September 19, 1933, after the observational work was completed and after most of the data had been reduced, the unit of electromotive force of the Bureau of Standards was increased by five microvolts, thus decreasing the values assigned to individual cells by this amount. This change is smaller than the experimental error of this investigation so that the values have not been revised to take account of this change.

TABLE 15.—*Data and results on the absolute determination of the ampere*

[All final runs have been included]

Date	Coil combination[1]	Temperature of coils: Fixed; average of two	Temperature of coils: Moving	Observed doubled force	Correction for: Temperature	Correction for: Load and leads	Doubled force corrected to 22 C and no load	Values of the current: I_A	Values of the current: I_{BS}	$\frac{I_{BS}-I_A}{I_A}$	Deviation from mean of set
		°C	°C	Grams	Milligram	Milligram	Grams	Absolute amperes	B.S. int. amperes	Parts per million	Parts per million
1927											
Feb. 12	L4 L3 M2	23.35	21.90	5.99868	+0.41	−0.23	5.99886	0.767638	0.767701	82	−8
15	do	23.38	22.04	810	.37	−.23	824	598	662	83	−7
Mar. 8	do	23.33	22.00	931	.37	−.23	945	675	743	89	−1
22	do	23.39	22.03	903	.38	−.23	918	658	725	87	−3
24	do	23.34	22.01	896	.37	−.23	910	653	727	96	+6
25	do	23.34	22.03	906	.37	−.23	920	660	727	87	−3
26	do	23.29	22.00	977	.36	−.23	990	704	776	94	−4
28	do	23.33	21.98	955	.38	−.23	970	691	751	78	−12
28	do	23.33	21.98	885	.38	−.23	6.00000	711	786	98	+8
29	do	25.28	23.80	978	.40	−.23	5.99995	707	786	103	+13
30	do	25.21	23.76	946	.39	−.23	962	686	761	98	+8
31	do	27.98	26.42	946	.40	−.23	963	687	762	98	+8
Apr. 1	do	28.20	26.42	946	.46	−.23	969	691	761	91	+1
2	do	23.39	22.00	961	.39	−.23	977	696	761	85	−5
2	do	23.39	22.00	895	.39	−.23	911	654	724	91	+1
5	do	23.28	21.93	899	.38	−.23	914	656	724	88	−2
5	do	23.35	21.95	856	.39	−.23	872	629	693	83	−7
	Average of 17 runs									90	±6
1930											
Aug. 25	S1 S2 M3	25.41	25.86	3.91376	−.05	0	3.91371	0.678650	0.678687	55	+2
26	do	25.43	25.86	373	−.04	0	369	648	687	58	+5
28	do	25.45	26.04	310	−.07	0	303	591	629	56	+3
Sept. 3	do	25.67	25.58	364	+.04	+.01	369	648	684	53	0
4	do	25.36	25.58	367	−.01	.01	367	646	686	59	+6
5	do	25.39	25.60	369	−.01	.01	369	648	685	55	+2
8	do	24.63	24.77	369	0	.01	370	649	686	55	+2
8	do	24.61	24.76	372	0	.01	373	652	686	50	−3
10	do	24.56	24.73	369	−.01	.01	369	648	684	53	0
10	do	24.54	24.70	371	−.01	.01	371	650	684	50	−3
11	do	24.55	24.71	370	−.01	.01	370	649	684	52	−1
11	do	24.56	24.70	371	0	.01	371	650	684	50	−3
15	do	24.75	24.82	366	+.01	+.04	371	650	684	50	−3
15	do	24.75	24.81	368	+.01	.04	373	652	684	47	−6
	Average of 14 runs									53	±3
1931											
Feb. 17	L3 L4 M2	24.85	23.55	4.68254	+.27	−.08	4.68273	0.678221	0.678294	107	+7
18	do	24.77	23.68	261	.23	.08	276	224	293	102	+2
21	do	24.75	23.48	262	.26	.08	280	227	294	99	−1
25	do	24.85	23.60	262	.26	.08	280	227	294	99	−1
Mar. 17	do	26.97	25.51	256	.29	.08	277	224	294	103	+3
20	do	27.02	25.44	256	.32	.08	280	227	293	97	−3
Apr. 3	do	23.65	22.45	266	.26	.08	284	230	293	93	−7
8	do	25.69	24.23	260	.30	.08	282	228	294	97	−3
	Average of 8 runs									100	±3
Mar. 23	L3 L4 M2	22.81	22.01	2.63906	+.10	−.02	2.63914	0.509159	0.509205	90	
30	do	22.58	21.85	909	+.09	−.02	916	161	205	86	
	Average of 2 runs									88	
Apr. 2	L3 L4 M2	26.79	23.92	10.55022	+1.38	−.53	10.55107	1.018052	1.018155	101	
17	do	28.92	25.92	25	1.42	.53	114	57	152	94	
24	do	28.91	25.93	20	1.41	.53	108	53	154	99	
	Average of 3 runs									98	

[1] In each case the first coil listed is the upper fixed coil.

TABLE 15.—*Data and results on the absolute determination of the ampere*—Contd.

[All final runs have been included]

Date	1 Coil combination[1]	2 Temperature of coils: Fixed; average of two	3 Temperature of coils: Moving	4 Observed doubled force	5 Correction for: Temperature	6 Correction for: Load and leads	7 Doubled force corrected to 22 C and no load	8 Values of the current: I_A	9 Values of the current: I_{BS}	10 $\frac{I_{BS}-I_A}{I_A}$	11 Deviation from mean of set
1932		°C	°C	Grams	Milligram	Milligram	Grams	Absolute amperes	B.S. Int. amperes	Parts per million	Parts per million
Jan. 7	S2 S1 M2	25.03	23.90	11.91728	+.61	−.27	11.91761	1.017659	1.017664	5	−4
11	do	24.86	23.78	724	.58	−.27	755	656	665	9	0
12	do	24.93	23.84	719	.59	−.27	751	655	664	9	0
18	do	25.75	24.64	723	.56	−.27	752	655	665	10	+1
19	do	25.36	24.21	718	.61	−.27	752	655	665	10	+1
23	do	25.42	24.25	726	.62	−.27	761	659	666	7	−2
25	do	25.51	24.34	726	.61	−.27	760	658	669	11	+2
25	do	25.51	24.35	730	.60	−.27	763	660	669	9	0
26	do	25.43	23.65	681	1.04	−.27	758	657	669	12	+3
28	do	24.65	24.32	782	.08	−.27	763	660	670	10	+1
29	do	25.60	24.74	745	.39	−.27	757	657	668	11	+2
	Average of 11 runs									9	±2
30	S2 S1 M2	23.30	23.24	5.29360	−.02	−.05	5.29353	0.678235	0.678240	7	+1
Feb. 9	do	22.14	22.16	363	−.01	−.05	357	238	241	4	−2
9	do	22.14	22.14	362	0	−.05	357	238	241	4	−2
15	do	22.35	22.27	354	+.01	−.05	350	234	241	11	+5
20	do	22.44	22.42	361	−.02	−.05	354	236	241	7	+1
22	do	22.46	22.61	365	−.06	−.05	354	236	241	7	+1
27	do	22.60	22.82	365	−.08	−.05	352	235	241	9	+3
29	do	23.36	23.01	350	+.07	−.05	352	235	240	7	+1
Mar. 7	do	22.55	22.11	349	+.11	−.05	360	240	239	−1	−7
8	do	23.50	22.90	345	+.14	−.05	359	230	239	0	−6
	Average of 10 runs									6	±3
12	S2 S1 M2	22.82	22.50	2.95985	+.04	−.01	2.95988	0.507160	0.507165	10	
14	do	21.52	21.28	985	+.05	−.01	989	161	165	9	
15	do	21.55	21.61	990	0	−.01	989	161	165	9	
	Average of 3 runs									9	
Apr. 5	L3 L4 M3	24.85	24.25	3.74713	+.13	−.10	3.74716	0.678318	0.678369	75	−7
9	do	24.55	24.48	718	+.05	−.10	713	315	370	81	−1
11	do	24.32	24.14	715	+.06	−.10	711	313	369	83	+1
12	do	24.29	24.17	654	+.05	−.10	649	258	314	83	+1
18	do	23.21	23.13	719	+.03	−.10	712	314	370	83	+1
19	do	23.20	23.19	717	+.02	−.10	709	311	370	87	+5
19	do	23.20	23.21	720	+.02	−.10	712	314	370	83	+1
23	do	23.26	23.30	724	+.01	−.10	715	317	370	78	−4
23	do	23.26	23.31	690	+.01	−.10	681	286	342	83	+1
25	do	23.22	23.67	697	−.04	−.10	683	288	343	81	−1
26	do	23.22	23.77	698	−.05	−.10	683	288	342	80	−2
	Average of 11 runs									82	±2
May 2	L3 L4 M3	26.76	26.70	8.43070	+.20	−.48	8.43042	1.017435	1.017524	87	+3
10	do	26.94	26.51	3064	.32	−.48	3048	438	526	87	+3
12	do	26.99	26.24	3056	.42	−.48	3050	440	526	85	+1
16	do	26.93	26.17	3061	.42	−.48	3055	444	528	83	−1
17	do	26.91	26.19	3060	.41	−.48	3053	442	528	85	+1
26	do	27.11	26.72	2994	.32	−.48	2978	398	484	85	+1
27	do	27.02	26.62	2998	.32	−.48	2982	400	484	83	−1
June 4	do	27.37	26.58	2992	.45	−.48	2989	403	487	83	−1
6	do	27.35	26.58	2995	.44	−.48	2991	405	489	83	−1
7	do	27.36	26.65	2996	.43	−.48	2991	405	487	81	−3
8	do	27.07	26.57	3003	.35	−.48	2990	404	488	83	−1
9	do	27.02	26.40	2995	.39	−.48	2986	402	488	85	+1
10	do	27.03	26.40	2999	.37	−.48	2988	403	488	84	0
10	do	27.03	26.39	3074	.37	−.48	3063	448	535	86	+2
	Average of 14 runs									84	±2

[1] In each case the first coil listed is the upper fixed coil.

TABLE 15.—*Data and results on the absolute determination of the ampere*—Contd.

[All final runs have been included]

Date	1 Coil combination[1]	2 Temperature of coils: Fixed; average of two	3 Temperature of coils: Moving	4 Observed doubled force	5 Correction for: Temperature	6 Correction for: Load and leads	7 Doubled force corrected to 22 C and no load	8 Values of the current: I_A	9 Values of the current: I_{BS}	10 $\frac{I_{BS}-I_A}{I_A}$	11 Deviation from mean of set
1932		°C	°C	Grams	Milligram	Milligram	Grams	Absolute amperes	B.S. Int. amperes	Parts per million	Parts per million
June 23	L3 L4 M3	24.20	24.26	2.08778	+.01	−.02	2.08777	0.506318	0.506357	77	0
24	do	24.17	24.24	778	+.01	−.02	777	318	357	77	0
24	do	24.17	24.24	781	+.01	−.02	780	322	361	77	0
24	do	24.17	24.25	789	+.01	−.02	788	330	372	83	+5
29	do	25.39	25.45	776	+.02	−.02	776	317	356	77	0
29	do	25.39	25.45	778	+.02	−.02	778	319	356	73	−4
	Average of 6 runs									77	±2
Oct. 25	S2 S1 M2	27.20	26.04	11.92045	+.45	−.32	11.92058	1.017786	1.017805	19	+4
26	do	27.20	25.95	1762	+.55	−.32	1785	770	683	13	−2
Nov. 1	do	25.59	24.51	1759	+.53	−.32	1780	665	683	18	+3
1	do	25.60	24.52	1761	+.53	−.32	1782	667	683	16	+1
8	do	25.52	24.35	1751	+.60	−.32	1779	664	683	19	+4
14	do	25.50	24.42	1786	+.54	−.32	1808	679	687	8	−7
	Average of 6 runs									15	±4

[1] In each case the first coil listed is the upper fixed coil.

A summary of the results of the measurements with the four sets of coils is given in table 16. The first three columns are self-explanatory. In column 4 are given the averages, for each combination of coils, of the mean results, as recorded in column 10 of table 15, for that combination. Each number in column 4 is subtracted from unity to obtain the numbers which are given in column 5, each number expressing, for any current, the ratio of its value in absolute amperes to its value in B.S. international amperes. The mean of these values, each weighted as indicated in column 6, is the final result of this investigation. The numbers in column 6 for weighting the values in column 5 are approximately proportional to the reciprocals of the average indicated error for each coil combination as given in table 14. Since only for one coil combination was the indicated error appreciably different from the others, only this combination was given a low weight. The difference between the final result and the value for each set of coils is given in column 7.

TABLE 16.—*The average results with each combination of coils*

1 Fixed coils	2 Moving coil	3 Number of independent observations	4 $\frac{I_{BS}-I_A}{I_A}$	5 Ratio of values of a current in Absolute Amperes to the value in B.S.Int. Amperes	6 Weight	7 Deviation from weighted mean
L3 L4	M3	31	81×10^{-6}	0.999919	5	-9×10^{-6}
L3 L4	M2	30	94	.999906	5	−22
S1 S2	M3	14	53	.999947	5	+19
S1 S2	M2	30	10	.999990	1	+62
Weighted means				.999928		$\pm20\times10^{-6}$
Probable error of weighted mean						$\pm8\times10^{-6}$

The result of this investigation may be expressed by stating that a current which has a value of 1 B.S. international ampere has a value of 0.999928 absolute ampere. This may be expressed by the equality

1 B.S. International Ampere = 0.999928 Absolute Ampere

The authors estimate that this result differs from the true value by less than 20 parts in a million.

The result obtained by Rosa, Dorsey, and Miller in 1911 may be expressed [44] as

1 B.S. international ampere = 0.999926 absolute ampere

The close agreement between the results (two parts in a million) is fortuitous, since the difference between the results is less than the probable error of either. The recent measurements [45] with the silver voltameter also indicate that there has been no important change in the unit of current at the Bureau of Standards since 1911.

A recent estimate [46] of the value of the B.S. international ohm in absolute measure is

1 B.S. international ohm = 1.000460 absolute ohms

From this estimate and the results on the determination of the ampere here reported, the value of any electrical quantity can be estimated in absolute units from its value as measured in international units. For example:

1 B.S. international volt = 1.000388 absolute volts
1 B.S. international watt = 1.000316 absolute watts

VIII. DISCUSSION OF RESULTS

The results on the ratio of the radii were self-checking, as shown in table 10, where the possible errors in the measurements on the coils are indicated. The largest indicated error in the ratio of the radii affects the absolute value of the current as measured with any coil combination by only a few parts in a million. The observed difference in the results obtained with different coil combinations is much larger than can be accounted for in that way.

The uniformity of the results in the absolute value of the current obtained on different days with a given coil combination, as shown in column 10 of table 15, indicates that the weighings and reduction to standard conditions caused an error of only six parts in a million in the most unfavorable case. In the cases where the coils were twice assembled in the balance, the results from the two assemblies differed by 5 and 7 parts in a million, respectively. This shows that errors in the adjustments of the coils did not cause all of the observed differences.

The observed difference between the mean of all the results and the result with any one coil combination might be explained by assuming that there is an error in the cross-sectional dimensions of one of the coils. However, no reasonable assumption concerning the errors in the cross sections of the coils will bring the results with the different

[44] In that work the result was stated in terms of the electromotive force of the Weston normal cell at 20 C. The value obtained was 1.018225 semiabsolute volts, a semiabsolute volt being the potential drop produced by 1 absolute ampere in a resistance of 1 B.S. international ohm. The Weston normal cell at 20 C. has, by international agreement, a value of 1.018300 international volts. Since, for two systems of units which have the same unit of resistance, the units of current and the units of electromotive force are directly proportional, the value obtained in 1911 for the ratio of the international to the absolute ampere is 1.018225/1.018300=0.999926.

[45] G. W. Vinal, International comparison of electrical units, B.S. Jour. Research, vol. 8, p. 729, 1932.

[46] See p. 92 of paper referred to in footnote 10.

coil combinations into substantially better agreement. Another possible explanation of the variation in the results when different coil combinations were used is that the coil windings did not strictly conform to the conditions assumed in deriving the theoretical formula. This can be tested by using a different type of coil. At present there is no satisfactory explanation of the rather large discrepancy in results with different coil combinations. It may be noted, however, that observations with the coil combination S1 S2 M3 were made under less favorable conditions than the others. The work was done in the late summer when the humidity was high and the electrical measurements were difficult. The result with the coil combination S1 S2 M2 differs from the mean by a much larger amount than any other coil combination. That combination was not used in 1911, probably because the computation of the force by the formulas then available would have been very laborious. As the computation can be readily made by the formula now in use, there seemed to be no reason why that combination should not be used in this investigation. The reason why the result with that combination is so different from the others has not been found, and nothing has been discovered that would justify the discarding of the value. The low weighting of the result for that combination is justified because the weighting factors were deduced from an entirely independent set of measurements.

The authors are of the opinion that, to obtain a more accurate result for the absolute value of the ampere, the present current balance should be improved and some entirely different method [47] should be perfected in which the systematic errors would probably be quite different from those in the current-balance method. The most obvious improvement of the current balance is the construction of new coils, the cross sections of which can be more accurately measured and the windings of which conform more nearly to the conditions assumed in deriving the equation for the force.

The authors wish to express their indebtedness to many members of the staff of this Bureau for the helpful cooperation without which this work would have been much more difficult. The resistance section and the electrochemical section made many tests of resistance coils and standard cells. N. P. Case gave assistance in the design and setting-up of much of the apparatus; G. B. Schubauer made the earlier measurements with the current balance, and V. H. Goerke made most of the measurements of the ratio of the radii of the coils.

WASHINGTON, March 24, 1934.

[47] See footnote 11 p. 668.

NOTE.—After the manuscript of the above paper was sent to press decision was reached to use the name National Bureau of Standards (abbreviated NBS) instead of Bureau of Standards, (abbreviated B.S.) as given in this paper.

U.S. DEPARTMENT OF COMMERCE BUREAU OF STANDARDS

RESEARCH PAPER RP686

Part of Bureau of Standards Journal of Research, vol. 12, June 1934

CALORIMETRIC DETERMINATION OF THE HEATS OF COMBUSTION OF ETHANE, PROPANE, NORMAL BUTANE, AND NORMAL PENTANE

By Frederick D. Rossini

ABSTRACT

The present investigation on the calorimetric determination of the heats of combustion of ethane, propane, normal butane, and normal pentane was undertaken because of the dearth of information concerning these thermochemical constants for which there is pressing need in industry and in the sciences.

The data of the present investigation give for the heats evolved in the combustion in oxygen, at a temperature of 25 C and a constant pressure of 1 atmosphere, of gaseous ethane, gaseous propane, gaseous normal butane, and gaseous normal pentane, respectively, to form gaseous carbon dioxide and liquid water, the following values, in international kilojoules per mole: Ethane, $1{,}559.57 \pm 0.44$; propane, $2{,}219.57 \pm 0.51$; normal butane, $2{,}877.88 \pm 0.63$; normal pentane, $3{,}536.00 \pm 0.88$. Converted to k-cal$_{15}$ by means of the factor 1.00040/4.1850, these values become, in k-cal$_{15}$ per mole: Ethane, 372.81 ± 0.11; propane, 530.57 ± 0.12; normal butane, 687.94 ± 0.15; normal pentane, 845.27 ± 0.21.

The hitherto "best" values for the heats of combustion of these gases differ from the values obtained in the present investigation by the following amounts Ethane, -1.23 percent; propane, -0.87 percent; normal butane, no existing data; normal pentane, -0.86 percent. These differences are from 30 to 50 times the estimated uncertainties in the values from the present investigation.

CONTENTS

		Page
I.	Introduction	736
II.	Units, atomic weights, etc	736
III.	Method and apparatus	737
IV.	Chemical procedure	739
	1. Preparation and purity of the hydrocarbons	739
	2. Purity of the combustion reaction	741
	3. Determination of the amount of reaction	742
V.	Calorimetric procedure	742
	1. Electrical energy experiments	742
	2. Correction experiments	743
	3. Reaction experiments	744
VI.	Results of the present investigation	746
VII.	Data of previous investigations	747
	1. Ethane	747
	2. Propane	747
	3. Normal butane	748
	4. Normal pentane	748
VIII.	Summary	749
IX.	References	750

I. INTRODUCTION

Accurate values for the heats of combustion of ethane, propane, normal butane, and normal pentane are needed for the following reasons: First, ethane, propane, and butane are becoming increasingly important as fuel gases in industry and in the home; second, for these substances, values of the free energies of formation, which are needed for computing chemical equilibria in which these gases take part, can be determined accurately only from the relation involving entropies and heats of formation, which latter values are calculated from the heats of combustion; and third, accurate values for the heats of combustion of the normal paraffin hydrocarbon gases will give data from which may be drawn information concerning the energies of the atomic linkages in these molecules.

The existing data on the heats of combustion of ethane, propane, butane, and pentane are very meager and, according to present standards, exceedingly uncertain. For ethane and propane there are the discordant values of Thomsen (1)[1] and Berthelot and Matignon (2), who used the calorimetric equipment available half a century ago and who had not pure gases to work with. For normal butane, there are no data on the heat of combustion recorded in the literature. For normal pentane there exists the value obtained by Roth and Machlett (3), who published no report of their experiments but gave simply the numerical results.

Because of the dearth of information concerning the heats of combustion of these gases and because of the pressing need in industry and in the sciences for accurate values concerning them, the present investigation on the calorimetric determination of the heats of combustion of ethane, propane, normal butane, and normal pentane was undertaken.

II. UNITS, ATOMIC WEIGHTS, ETC.

The fundamental unit of energy employed in the present calorimetric experiments is the international joule based upon standards of emf and resistance maintained at this Bureau (4). Recent experimental work in this Bureau (13) on the relation between the international and the absolute units of current and resistance indicates the relation between the absolute joule and the international joule, derived from standards maintained at this Bureau, to be 1 international (Bureau of Standards) joule = 1.00032 absolute joules. But for the sake of consistency the relation which has heretofore been used for converting the data obtained in the thermochemical laboratory of the Bureau of Standards will be used in the present and succeeding papers, until such time as the relation between the absolute and the international joule will be fixed by international accord. At that time, all the data that will have been obtained in this thermochemical laboratory will be converted to the new basis.

The conversion factors used throughout this paper are:

1 international joule = 1.00040 absolute joules

1 g-cal$_{15}$ = 4.1850 absolute joules

[1] The numbers in parentheses, here and throughout the text, refer to the references, p. 750.

The atomic weights of oxygen, hydrogen, and carbon are taken from the 1934 report of the International Committee on Atomic Weights (5): Oxygen, 16.0000; hydrogen, 1.0078; carbon, 12.00. As explained in section IV, part 3, of this paper, the thermal data obtained in the present investigation are independent of the atomic weight of carbon, the number of moles of hydrocarbon involved in the calorimetric experiments having been determined from the mass of water formed.

III. METHOD AND APPARATUS

The general calorimetric method employed in the present investigation is the same as that previously used in this laboratory in the determination of the heats of formation of water and hydrogen chloride and the heats of combustion of methane, carbon monoxide, methanol, and ethanol (6); and is, briefly, a substitution method in which the heat evolved by a measured amount of the chemical reaction is found to be equivalent to the heat evolved by a measured amount of electrical energy, the calorimeter serving as the comparator. Unless otherwise stated the procedure and the nomenclature follow the previous investigations (6).

For the combustion of ethane, it was found that the reaction vessel used for the combustion of methane served very well, provided that the proper conditions prevailed with respect to the rates of flow of the ethane and the oxygen. This reaction vessel has already been described (6).

For the combustion of propane, normal butane, and normal pentane a new reaction vessel was designed, in which provision was made for aspirating oxygen into the stream of hydrocarbon gas before it reached the burner tip.[2] A cross section of this new reaction vessel [3] is shown in figure 1. A is the tube through which the oxygen enters the reaction chamber; B is the tube through which the hydrocarbon gas passes to the burner tip F where, having been ignited by sparks across the gap between the ends of the platinum wires D, it burns with a flame; at E is the injector by means of which oxygen is drawn into the stream of hydrocarbon gas; at G is collected as a liquid most of the water formed in the combustion; and the exit gases leave the reaction vessel through the tube C.

The dimensions of the new reaction vessel necessitated the building of a new heating coil to fit it. A thin copper cylinder, 5 cm long and 7.5 cm in diameter, was coated on the outside with a layer of pizein cement; around this cylinder was wound, noninductively, about 65 ohms of enameled constantan wire (no. 30, B. & S. gage); enameled copper leads were soldered to the ends of the constantan wire and insulated with pizein on the cylinder; and the outside of the cylinder was covered with another coating of pizein.

[2] The author is indebted to Francis A. Smith for valuable advice in the design of the burner.

[3] This reaction vessel was built by E. O. Sperling, and the author is indebted to him for improvements in the design.

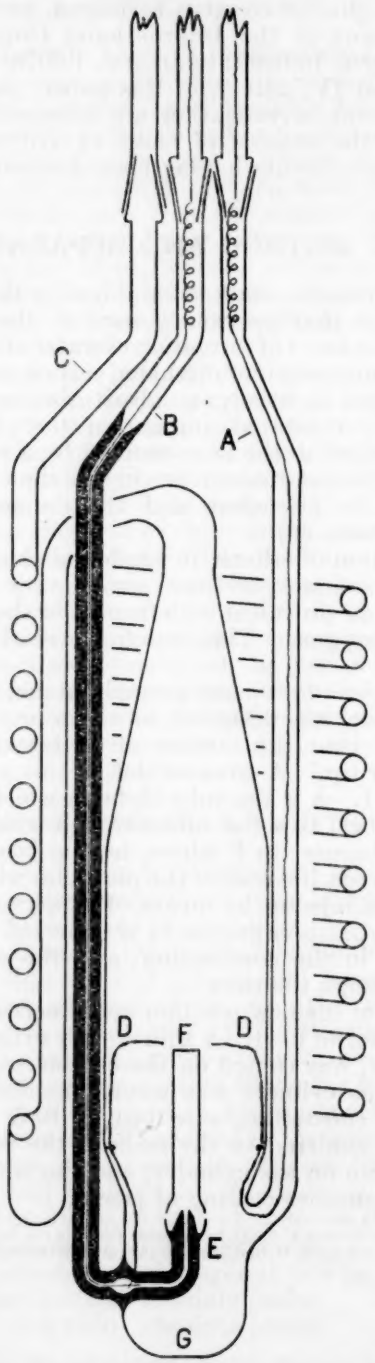

FIGURE 1.—*Crosssection of the reaction vessel used in the combustion of propane, butane, and pentane.*

The description is given in the text. The drawing is made to scale, and the over-all length is 26 cm.

IV. CHEMICAL PROCEDURE

1. PREPARATION AND PURITY OF THE HYDROCARBONS

In the present experiments the amount of reaction was determined from the mass of water formed. Because the heats of combustion of these hydrocarbons per mole of water formed are not greatly different, quite an appreciable amount of a homologous impurity may be contained in a given sample without necessitating any significant correction to the observed heat effect. For example, if a sample of normal butane contains as impurity 0.2 mole percent of propane, the observed heat effect will be less than that for pure normal butane by 0.006 percent. Table 1 gives the amounts of various impurities necessary to cause an error of ± 0.01 percent in the heat of combustion.

TABLE 1.—*The effect of impurities on the heat of combustion*

Substance	Impurity	Amount of impurity necessary to cause an error of 0.01 percent in the heat of combustion	Error in the heat of combustion
		Mole percent	*Percent*
Ethane	Methane	0.10	−0.01
	Propane	.11	+.01
Propane	Ethane	.21	−.01
	Butane	.21	+.01
Normal butane	Propane	.35	−.01
	Pentane	.35	+.01
Normal pentane	Butane	.57	−.01
	Hexane	.57	+.01

The samples of ethane, propane, and normal butane used in the present investigation were prepared to our order by the laboratory of the Linde Air Products Co., Buffalo, N.Y. These saturated hydrocarbons were obtained from natural gas by repeated fractional distillation at low temperatures. The manner of purification was such that each gas was expected to contain less than 0.2 percent by volume of impurity, which impurity would be a homologous substance, as for example, an impurity of ethane or butane in the sample of propane. Subsequent tests made in our laboratory indicated that the amount of impurity in the various samples was, in general, considerably less than 0.2 percent. About 2.4 moles of each gas was placed in highly evacuated steel cylinders, which were fitted with good valves and had internal volumes of about 2.8 liters.

In our laboratory, the ethane, propane, and normal butane were examined for impurities by Martin Shepherd (7), who separated, by isothermal distillation at low pressures, a sample of each gas into three fractions, and measured the difference in the vapor pressures of the middle cut and the initial distillate and of the middle cut and the final residue. The amounts of the initial distillate and the final residue were each less than 1/20 of the entire sample, and the difference in vapor pressures was measured by a differential manometer sensitive to ± 0.02 mm of Hg. The data obtained by Shepherd are given in table 2, where Δp is the difference between the vapor pressures, measured at the temperature t, of the middle cut and the initial distillate or the final residue, and ΔX_B, (see (7) for method of calculation and exact definition of terms), represents approx-

TABLE 2.—*Data on the purity of the ethane, propane, and normal butane, as shown by measurement of the difference in the vapor pressures between the middle cut and the initial distillate and the final residue, respectively*

Initial distillate [1]				Final residue [1]		
Substance	Δp	t	ΔX_B	Δp	t	ΔX_B
	mm Hg	°C	*Mole fraction*	*mm* Hg	°C	*Mole fraction*
Ethane	0.29	−189.1	0.009 methane	0.01	−150.0	0.005 propane.
Propane	.00	−58.2	(0.00001 ethane	.02	−49.3	0.00004 normal or isobutane.
Normal butane	7.82	.0	0.003 propane 0.020 isobutane	.22	.0	0.00035 normal pentane.

[1] The amounts of the initial distillate and the final residue were respectively less than 1/20 of the entire sample. The value of ΔX_B gives approximately the mole fraction of the given impurity in the initial distillate or the final residue, not in the entire sample. The values of Δp were read to ±0.02 mm Hg.

imately the mole fraction of a possible impurity, B, present in the initial distillate or the final residue. The mole fraction of the impurity B in the entire sample would be about 1/20 of the value of ΔX_B given in table 2, were it not for the fact that the isothermal distillation does not isolate all of the impurity in the initial distillate or the final residue. Assuming, as a probable case, that one half of the impurity is obtained in the initial distillate or the final residue, then the mole fraction of the impurity B in the entire sample would be about 1/10 the value of ΔX_B.

The normal pentane used in the present experiments was from the lot prepared synthetically by Mair (8), who gave a complete report of its preparation and properties. The following are some of the physical constants of the normal pentane: boiling point at 760 mm Hg, 36.06 degrees C; freezing point in air, −129.73 degrees C; freezing range of the sample, 0.026° C; refractive index, N_D^{25}, 1.35470.

TABLE 3.—*Results of the analytical experiments for determining the ratio of carbon to hydrogen in the ethane, propane, normal butane, and normal pentane*

Substance	Number of experiments	Average amount of hydrocarbon used in each experiment	Ratio	Average value of the ratio	Average deviation from the mean	Maximum deviation from the mean
		Mole				
Ethane	5	0.049	6C/2H	0.99992	±0.00018	0.00039
Propane	7	.034	8C/3H	1.00016	±.00019	.00034
Normal butane	6	.025	10C/4H	1.00014	±.00012	.00028
Normal pentane	6	.019	12C/5H	.99994	±.00022	.00041

In table 3 are given the results of experiments on the determination of the ratio of carbon to hydrogen in the ethane, propane, normal butane, and normal pentane. In these experiments the combustion was carried out in the calorimetric reaction vessel and the analytical procedure was the same as that used for methane (6). The amount of carbon dioxide collected in these experiments was corrected, when necessary, for the small amounts of carbon monoxide formed. (See p. 741.)

From the foregoing data, it appears that the purity of the ethane, propane, normal butane, and normal pentane used in the present investigation was such that, per mole of water formed, the heats of combustion of these samples would differ from the heats of combustion of the absolutely pure hydrocarbons by less than 0.01 percent.

2. PURITY OF THE COMBUSTION REACTION

The purity of the combustion reaction was examined as reported in previous papers.

A new supply of oxygen, prepared commercially from liquid air, was obtained for the present experiments. This oxygen, like that previously used, was low in inert gases (0.6 mole percent) and was similarly purified. A flow of oxygen considerably in excess of the stoichiometric requirements for complete combustion was used in all the experiments.

The combustion of ethane was carried out in the reaction vessel used for methane and other gases (6). It was necessary to use such a rate of flow of the ethane as would give a flame with a blue mantle, a sign of practically complete combustion, and which was sufficiently removed from the burner tip to prevent decomposition (with consequent deposition of carbon on the quartz tip) of the ethane before it reached the flame proper. The desired ethane flame was about 1.5 cm long. In the combustion of the ethane under these conditions, it was found that, on the average, 0.008 percent of the carbon in the sample was burned to carbon monoxide instead of carbon dioxide. This necessitated a correction of + 0.003 percent to the observed heat effect in the calorimetric reaction experiments, and of + 0.008 percent to the observed mass of carbon dioxide in the analytical experiments on the ratio of carbon to hydrogen in the ethane.

For the combustion of the propane and normal butane, the reaction vessel shown in figure 1 was used. The aspiration of oxygen into the stream of hydrocarbon gas before it reached the flame made possible the combustion of these hydrocarbons without deposition of carbon on the burner tip. The amount of oxygen aspirated into the stream of hydrocarbon gas was kept below that amount which would cause the flame to flash back to the capillary jet, by governing the size of the injector holes and the rate of flow of the hydrocarbon gas. In the combustion experiments with propane and normal butane burned in this manner, with a blue flame about 1.5 cm long, no carbon monoxide was detected in the exit gases.

The combustion of the normal pentane, which was carried as a gas into the reaction vessel by means of a stream of nitrogen, was performed in the same reaction vessel that was used for propane and butane. The composition of the gaseous mixture of nitrogen and pentane was about 0.65 mole of normal pentane to 0.35 mole of nitrogen. The nitrogen was bubbled through the liquid normal pentane at a temperature of 24 C and then the mixture passed through ascarite, magnesium perchlorate, and phosphorus pentoxide before arriving at the calorimeter. The pentane flame was blue and about the same size as for the other gases. The amount of carbon monoxide[4] formed in the combustion of the normal pentane in this manner was found to be 0.00020 mole per mole of carbon dioxide, which necessitated a correction of + 0.008 percent to the observed heat effect in the calorimetric reaction experiments, and a correction of + 0.020 percent to the observed mass of carbon dioxide in the analytical experiments on the ratio of carbon to hydrogen. The amount of nitrogen oxides in the exit gases from the combustion of pentane

[4] The tests for carbon monoxide were made in the gas section by Carroll Creitz.

was found to be 0.00004 mole per mole of carbon dioxide,[5] which necessitated no significant correction.

3. DETERMINATION OF THE AMOUNT OF REACTION

The amount of reaction in each calorimetric combustion experiment was computed from the mass of water formed, which was determined according to our usual procedure (6). In this connection it should be emphasized that for work of the highest precision the U-tube absorbers should be filled with hydrogen at the times of weighing, in order to make negligible any errors in corrections due to changes in the room temperature or the barometric pressure, and to make more certain the correction for the change in the volume of the solid absorbent.

In the present experiments 1 mole (18.0156 g) of H_2O was taken as equivalent to 1/3 mole of C_2H_6, to 1/4 mole of C_3H_8, to 1/5 mole of C_4H_{10}, or to 1/6 mole of C_5H_{12}. In this manner the values of the heats of combustion obtained in the present investigation are independent of the atomic weight of carbon.

In an auxiliary experiment an amount of the gaseous mixture of normal pentane and nitrogen containing 0.17 g of pentane was passed through a carefully weighed U-tube containing dehydrite (magnesium perchlorate trihydrate) and phosphorus pentoxide, and the change in mass of the U-tube was found to be zero ± 0.00005 g. This determination was necessary because, at the extinction of the pentane flame, there was always several mg of unburned pentane in the inlet tube, which pentane was later to be swept out through the U-tube.

V. CALORIMETRIC PROCEDURE

1. ELECTRICAL ENERGY EXPERIMENTS

The data of the experiments made to determine the electrical energy equivalent of the calorimeter system used for the combustion of ethane are given in table 4. (See (6) for nomenclature.) The "error" of the mean value of these experiments is

$$\pm\ 2\sqrt{\Sigma\Delta^2/n(n-1)} = \pm\ 0.012 \text{ percent},$$

where $\Sigma\ \Delta^2$ is the sum of the squares of the percentage deviations and n is the number of experiments.[6]

The data of the experiments made to determine the electrical energy equivalent of the calorimeter system used in the combustion of propane, normal butane, and normal pentane are given in table 5. The "error" of the mean value of these experiments is

$$\pm\ 2\sqrt{\Sigma\Delta^2/n(n-1)} = \pm\ 0.008 \text{ percent}$$

[5] The test for nitrogen oxides was made in the reagents and platinum metals section by F. W. Schwab.
[6] This formula gives an "error" that is three times as large as that obtained with the usual formula for the "probable error" of the mean.

TABLE 4.—*Calorimetric results of the electrical energy experiments* [1] *for ethane*

Experiment no.	ΔR	k	K	U	$\Delta t_{corr.}$	Average temperature	Electrical energy [2]	Mass of calorimeter water	Electrical energy equivalent of calorimeter system [3]	Deviation from mean
	Ohm	*Min*$^{-1}$	*Ohm*	*Ohm*	*Degrees C*	*Degrees C*	*Int. joules*	*g*	*Int. joules per degree C*	*Joules per degree C*
1	0.298843	0.001969	0.005401	0.000254	2.90636	25.10	44,944.5	3,625.40	15,441.8	1.5
2	.289622	.001943	.005885	.000110	2.81156	25.06	43,464.2	3,624.30	15,441.2	.9
3	.289200	.001937	.005867	.000046	2.80819	25.06	43,392.7	3,623.14	15,439.2	−1.1
4	.294777	.001948	.005835	−.000140	2.86566	25.09	44,257.4	3,621.44	15,438.3	−2.0
5	.296576	.001933	.005938	.000012	2.88097	25.09	44,539.5	3,624.94	15,439.4	−.9
6	.299513	.001946	.005366	−.000014	2.91601	25.10	45,038.2	3,620.49	15,443.2	2.9
7	.297286	.001942	.005430	.000007	2.89309	25.09	44,673.9	3,620.69	15,438.8	−1.5
8	.297230	.001935	.005355	.000048	2.89287	25.10	44,655.2	3,617.93	15,445.1	4.8
9	.296837	.001931	.005367	.000226	2.88709	25.10	44,563.2	3,619.94	15,435.7	−4.6
Mean									15,440.3	±2.2

[1] These experiments were performed in January 1933.
[2] The time of electrical energy input was 17 or 18 minutes, the current 0.78 to 0.83 ampere.
[3] Corrected to 3,620.00 g of water and an average temperature of 25.00 C.

TABLE 5.—*Calorimetric results of the electrical energy experiments* [1] *for propane, butane, and pentane*

Experiment no.	ΔR	k	K	U	$\Delta t_{corr.}$	Average temperature	Electrical energy [2]	Mass of calorimeter water	Electrical energy equivalent of calorimeter system [3]	Deviation from mean
	Ohm	*Min*$^{-1}$	*Ohm*	*Ohm*	*Degrees C*	*Degrees C*	*Int. joules*	*g*	*Int. joules per degree C*	*Joules per degree C*
1	0.410460	0.001932	0.007159	0.000156	3.99628	25.01	60,887.8	3,561.77	15,228.7	−1.4
2	.408615	.001934	.007255	.000166	3.97695	25.00	60,962.0	3,583.62	15,230.2	.1
3	.412305	.001904	.007074	−.000034	4.01730	25.01	61,097.8	3,554.76	15,230.6	.5
4	.411657	.001940	.007156	.000084	4.00893	25.03	60,991.1	3,555.93	15,230.8	.7
5	.411322	.001930	.007245	.000075	4.00479	25.01	60,950.2	3,557.44	15,230.0	−.1
6	.413270	.001925	.007277	.000053	4.02400	25.02	61,236.0	3,557.87	15,226.6	−3.5
7	.409501	.001934	.006995	−.000046	3.99049	25.00	60,814.1	3,563.15	15,226.9	−3.2
8	.410563	.001934	.006721	−.000223	4.00540	25.00	60,880.0	3,552.02	15,232.8	2.7
9	.409252	.001926	.006818	.000000	3.98923	25.00	60,705.9	3,556.92	15,230.3	.2
10	.408933	.001941	.007053	−.000093	3.98466	25.00	60,673.4	3,559.35	15,229.4	−.7
11	.410085	.001941	.006848	−.000055	3.99774	25.00	60,830.3	3,555.97	15,233.0	2.9
12	.407731	.001943	.006930	−.000190	3.97493	25.00	60,454.7	3,554.44	15,232.2	2.1
Mean									15,230.1	±1.5

[1] Experiments 1 to 6 were performed in September 1933, and experiments 7 to 12 in January 1934.
[2] The time of electrical energy input was 16 or 17 minutes, the current 0.95 to 1.00 ampere.
[3] Corrected to 3,560.00 g of water and an average temperature of 25.00 C.

2. CORRECTION EXPERIMENTS

The "spark" energy was determined calorimetrically to be 1.43 ± 0.06 joules per second for the experiments on ethane and 1.31 ± 0.06 joules per second for the experiments on propane, normal butane, and normal pentane.

The "gas" energy and the "vaporization" energy were determined as in the previous investigations (6).

As before (6), calorimetric experiments were performed in which a number of ignitions and extinctions of the flame occurred, the purpose being to subordinate, relatively, the heat evolved in the combustion of the hydrocarbon to the "spark", "gas", and "vaporization" energies. In each of these experiments thermal balance was obtained within the limits of error of the measurements.

3. REACTION EXPERIMENTS

The calorimetric data of the combustion experiments with ethane, propane, normal butane, and normal pentane are given in tables 6, 7, 8, and 9, respectively. The "errors" of the mean values of the combustion experiments on the various gases, computed as $\pm 2\sqrt{\Sigma\Delta^2/n(n-1)}$, are, respectively: Ethane, ± 0.023 percent; propane, ± 0.019 percent; normal butane, ± 0.018 percent; and normal pentane, ± 0.021 percent.

TABLE 6.—*Calorimetric results of the reaction experiments for ethane*

Experiment no.	ΔR	k	K	U	$\Delta t_{corr.}$	Average temperature
	Ohm	*Min*$^{-1}$	*Ohm*	*Ohm*	*Degrees C*	*Degrees C*
1	0.290372	0.001898	0.006838	−0.000069	2.81135	25.09
2	.294673	.001942	.005332	.000137	2.86687	25.08
3	.296344	.001923	.005790	.000020	2.88005	25.08
4	.298509	.001933	.005946	−.000156	2.90171	25.09
5	.295834	.001980	.006425	.000091	2.86800	25.08
6	.296406	.001957	.006635	−.000075	2.87323	25.08
7	.294781	.001945	.005662	−.000050	2.86652	25.08
Mean						

Experiment no.	Electrical energy equivalent of calorimeter system [1]	"Gas" energy	"Spark" energy	"Vaporization" energy	Mass of ethane	Heat [2] of combustion at 25 degrees C	Deviation from mean
	Int. joules per degree C	*Joules*	*Joules*	*Joules*	*Mole*	*Int. kilojoules per mole*	*Kilojoule per mole*
1	15,442.1	4.6	17.2	375.8	0.0280855	1558.74	−0.83
2	15,459.3	13.9	14.3	342.9	.0286407	1559.46	−.11
3	15,451.1	8.6	14.3	303.4	.0287294	1559.35	−.22
4	15,455.0	13.9	15.0	298.0	.0289423	1559.81	.24
5	15,456.9	5.9	22.9	331.7	.0286226	1559.84	.27
6	15,455.0	12.4	32.9	326.8	.0286718	1559.51	−.06
7	15,430.7	13.1	15.7	261.9	.0285167	1560.26	.69
Mean						1559.57	±.35

[1] Includes the heat capacity of ½ the mass of liquid water formed in the reaction.
[2] Includes a correction of +0.003 percent for the carbon monoxide formed.

TABLE 7.—*Calorimetric results of the reaction experiments for propane*

Experiment no.	ΔR	k	K	U	$\Delta t_{corr.}$	Average temperature
	Ohm	*Min*$^{-1}$	*Ohm*	*Ohm*	*Degrees C*	*Degrees C*
1	0.403093	0.001956	0.011899	−0.000179	3.87955	24.97
2	.412941	.001940	.015120	−.000008	3.94359	25.02
3	.411032	.001922	.007486	−.000011	4.00037	25.01
4	.413092	.001935	.008225	−.000008	4.01343	25.02
5	.409675	.001947	.007578	−.000081	3.98670	25.01
6	.406890	.001936	.007383	.000098	3.95925	24.99
7	.412252	.001948	.010572	.000027	3.98149	25.01
8	.409171	.001945	.008632	.000059	3.96987	25.00
Mean						

Experiment no.	Electrical energy equivalent of calorimeter system [1]	"Gas" energy	"Spark" energy	"Vaporization" energy	Mass of propane	Heat of combustion at 25 degrees C	Deviation from mean
	Int. joules per degree C	*Joules*	*Joules*	*Joules*	*Mole*	*Int. kilojoules per mole*	*Kilojoules per mole*
1	15,197.4	−4.0	57.6	451.2	0.0267306	2220.25	0.68
2	15,215.8	−8.3	68.2	340.5	.0271917	2219.34	−.23
3	15,231.2	4.8	24.9	260.5	.0275458	2220.69	1.12
4	15,230.8	6.9	32.7	294.6	.0276635	2219.40	−.17
5	15,223.6	−2.6	13.1	278.0	.0274649	2219.35	−.22
6	15,225.4	6.3	23.6	280.5	.0272818	2219.22	−.35
7	15,232.4	2.9	35.4	281.2	.0274421	2219.08	−.49
8	15,230.9	.6	19.7	257.8	.0273537	2219.20	−.37
Mean						2219.57	±.45

[1] Includes the heat capacity of ½ the mass of liquid water formed in the reaction.

TABLE 8.—*Calorimetric results of the reaction experiments for normal butane*

Experiment no.	ΔR	k	K	U	$\Delta t_{corr.}$	Average temperature
	Ohm	*Min*$^{-1}$	*Ohm*	*Ohm*	*Degrees C*	*Degrees C*
1	0.409115	0.001946	0.006179	−0.000048	3.99469	25.00
2	.410905	.001939	.006254	−.000024	4.01145	25.00
3	.409376	.001940	.006779	−.000074	3.99158	25.00
4	.411469	.001925	.006667	−.000053	4.01323	25.00
5	.411537	.001923	.006314	−.000041	4.01729	25.00
6	.409147	.001927	.006896	−.000139	3.98880	25.00
7	.411499	.001928	.006312	−.000170	4.01821	25.00
8	.410687	.001935	.006511	−.000142	4.00791	25.00
Mean						

Experiment no.	Electrical energy equivalent of calorimeter system [1]	"Gas" energy	"Spark" energy	"Vaporization" energy	Mass of normal butane	Heat of combustion at 25 degrees C	Deviation from mean
	Int. joules per degree C	*Joules*	*Joules*	*Joules*	*Mole*	*Int. kilojoules per mole*	*Kilojoules per mole*
1	15,254.0	6.9	7.9	221.7	0.0212578	2876.90	−0.98
2	15,260.4	4.0	14.4	207.3	.0213428	2877.49	−.39
3	15,208.5	7.4	23.6	236.3	.0211713	2877.80	−.08
4	15,224.6	4.6	17.0	221.9	.0213016	2878.17	.29
5	15,250.5	5.1	15.7	220.2	.0213528	2879.06	1.18
6	15,248.2	1.9	15.7	238.8	.0212144	2877.63	−.25
7	15,218.2	2.4	17.0	221.5	.0213140	2878.72	.84
8	15,222.1	2.4	14.4	216.6	.0212752	2877.23	−.65
Mean						2877.88	±.58

[1] Includes the heat capacity of ½ the mass of liquid water formed in the reaction.

TABLE 9.—*Calorimetric results of the reaction experiments for normal pentane*

Experiment no.	ΔR	k	K	U	Δt corr.	Average temperature
	Ohm	*Min*$^{-1}$	*Ohm*	*Ohm*	*Degrees C*	*Degrees C*
1	0.410430	0.001937	0.005964	−0.000108	4.01045	25.00
2	.409639	.001936	.006180	−.000134	4.00072	25.00
3	.407770	.001952	.007482	−.000213	3.97007	25.00
4	.409557	.001950	.006136	−.000106	4.00007	25.00
5	.411967	.001949	.005585	−.000127	4.02963	25.02
6	.409974	.001943	.006808	−.000122	3.99770	25.00
7	.413547	.001925	.006274	−.000046	4.03766	25.01
8	.410295	.001945	.006162	−.000094	4.00701	25.01
Mean						

Experiment no.	Electrical energy equivalent of calorimeter system [1]	"Gas" energy	"Spark" energy	"Vaporization" energy	Mass of normal pentane	Heat [2] of combustion at 25 degrees C	Deviation from mean
	Int. joules per degree C	*Joules*	*Joules*	*Joules*	*Mole*	*Int. kilojoules per mole*	*Kilojoules per mole*
1	15,180.4	4.0	9.8	211.0	0.0172803	3535.25	−0.75
2	15,230.2	2.8	21.6	251.2	.0172938	3537.05	1.05
3	15,229.6	4.0	14.4	350.5	.0172008	3535.15	−.85
4	15,222.7	6.2	17.0	229.0	.0172761	3537.54	1.54
5	15,258.6	−1.1	15.1	256.6	.0174528	3537.07	1.07
6	15,214.3	1.7	24.9	282.7	.0172768	3535.76	−.24
7	15,063.6	−2.5	22.3	255.6	.0172734	3534.76	−1.24
8	15,213.7	1.1	18.3	240.5	.0173076	3535.41	−.59
Mean						3536.00	±.92

[1] Includes the heat capacity of ½ the mass of liquid water formed in the reaction.
[2] Includes a correction of + 0.008 percent for the carbon monoxide formed.

VI. RESULTS OF THE PRESENT INVESTIGATION

The uncertainties in the final values obtained from the present data have been computed by taking the total percentage "error" as equal to $\pm\sqrt{e_1^2+e_2^2+e_3^2}$, where e_1 is the percentage "error" of the mean value of the calorimetric experiments with electrical energy, e_2 is the percentage "error" of the mean value of the calorimetric combustion experiments, and e_3 is an "error" of 0.01 percent assumed in the determination of the amount of reaction, due to impurities and other causes.

The data of the present investigation then yield for the heats of combustion, at a temperature of 25 C and a constant total pressure of 1 atmosphere, of gaseous ethane, gaseous propane, gaseous normal butane, and gaseous normal pentane, respectively, with gaseous oxygen to form gaseous carbon dioxide and liquid water, the following values, in international kilojoules per mole:

Ethane	1,559.57 ± 0.44
Propane	2,219.57 ± .51
Normal butane	2,877.88 ± .63
Normal pentane	3,536.00 ± .88

VII. DATA OF PREVIOUS INVESTIGATIONS

1. ETHANE

The existing data on the heat of combustion of ethane are those of Thomsen (1), and Berthelot and Matignon (2).

Thomsen performed seven experiments on ethane in his flame calorimeter at constant pressure and at an average temperature of 19 C. The first three experiments were made with a sample of ethane having the empirical formula $C_2H_{6.054}$, prepared from zinc ethyl and hydrochloric acid; the last four with a sample having the formula $C_2H_{6.033}$, prepared by the electrolysis of sodium acetate. Thomsen determined the amount of reaction from the mass of carbon dioxide formed. The writer has recomputed Thomsen's data, including a correction for an impurity of methane, and obtains from his work, for the heat of combustion of ethane at a temperature of 25 C and a constant pressure of 1 atmosphere, the value 368.9 ± 1.3 k-cal$_{15}$, or $1{,}543.2 \pm 5.5$ international kilojoules, per mole.

Berthelot and Matignon (2) performed three experiments on the heat of combustion of ethane, using a bomb calorimeter and working at an average temperature of 13 C. The amount of reaction was determined from the mass of carbon dioxide formed. Their recomputed data yield for the heat of combustion of ethane, at a temperature of 25 C and a constant pressure of 1 atmosphere, the value 372.1 ± 0.8 k-cal$_{15}$, or $1{,}556.6 \pm 3.4$ international kilojoules, per mole.

The various data on the heat of combustion of ethane are compared in figure 2. The values from Thomsen (1) and Berthelot and Matignon (2) are lower than the value from the present investigation by 1.05 and 0.19 percent, respectively.

2. PROPANE

The existing data on the heat of combustion of propane are those of Thomsen (1) and Berthelot and Matignon (2).

Thomsen performed seven experiments in his flame calorimeter, at constant pressure and at an average temperature of 17.8 C, on a sample of propane having the empirical formula $C_3H_{7.991}$, prepared from isopropyl iodide, zinc, and hydrochloric acid. The amount of reaction was determined from the mass of carbon dioxide formed. The recomputed data of Thomsen, including a correction for impurity, yield for the heat of combustion of propane, at a temperature of of 25 C and a constant pressure of 1 atmosphere, the value 528.7 ± 1.2 k-cal$_{15}$, or $2{,}211.7 \pm 5.0$ international kilojoules, per mole.

Berthelot and Matignon performed three experiments on propane in their bomb calorimeter at an average temperature of 17 C. The amount of reaction was determined from the mass of carbon dioxide formed. Their recomputed data yield for the heat of combustion of propane, at a temperature of 25 C and a constant pressure of 1 atmosphere, the value of 527.9 ± 1.8 k-cal$_{15}$, or 2208.4 ± 7.5 international kilojoules, per mole.

The various data on the heat of combustion of propane are compared in figure 2. The values from Thomsen (1), and Berthelot and Matignon (2) are lower than the value from the present investigation by 0.35 and 0.50 percent, respectively.

3. NORMAL BUTANE

There are no data on the heat of combustion of normal butane recorded in the literature.

4. NORMAL PENTANE

The only value for the heat of combustion of normal pentane recorded in the literature is that of Roth and Machlett (3). These

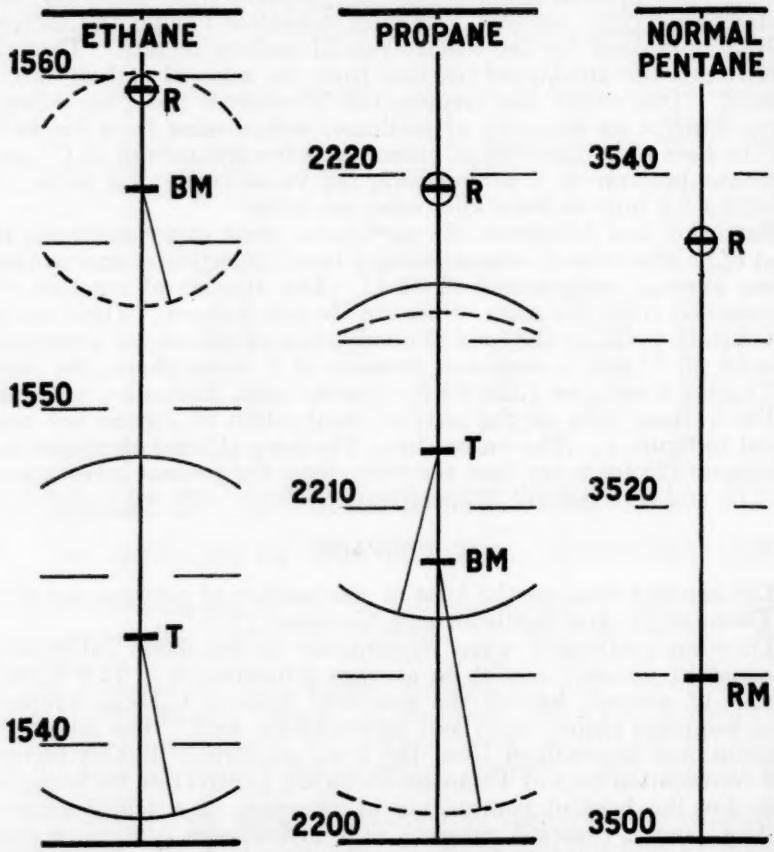

FIGURE 2.—*Plot of the various data on the heats of combustion of ethane, propane, and normal pentane.*

The ordinate scale gives the heat of combustion at a temperature of 25 C and a constant total pressure of 1 atmosphere in international kilojoules per mole. The average values of each investigation, together with the estimated uncertainties, are indicated as follows: T, Thomsen; BM, Berthelot and Matignon; RM, Roth and Machlett; R, Rossini.

authors have not published a report of their experiments, and give only the numerical result. Roth and Machlett found for the heat of combustion of liquid normal pentane, at constant volume in a bomb calorimeter at a temperature of 20 C, the value 11,551 g-cal_{15} per gram of liquid normal pentane, weighed in air. Applying the appropriate corrections, this value becomes 832.8 k-cal_{15} per true mole of liquid normal pentane, at a temperature of 25 C and a constant pressure of 1 atmosphere (lack of information prevents making the Washburn

correction). Roth and Machlett give for the heat of vaporization of liquid normal pentane at 20 degrees C the value 4.9 k-cal per mole. This value is apparently too low, as the calorimetric data of Griffiths and Awbery (9) yield 6.2 k-cal per mole for the heat of vaporization at 25 degrees C, and the data on the variation of the vapor pressure with temperature (10) yield 6.6 k-cal per mole. Taking the directly measured value of 6.2, the data of Roth and Machlett yield for the heat of combustion of gaseous normal pentane, at a temperature of 25 C and a constant total pressure of 1 atmosphere, the value 839.0 $k\text{-}cal_{15}$, or 3509.8 international kilojoules, per mole. If the value for the heat of vaporization given by Roth and Machlett were used, the above value would be lowered by 1.3 k-cal, or 5.4 kilojoules.

The data on the heat of combustion of gaseous normal pentane are compared in figure 2. The value from Roth and Machlett (3) is lower than that from the present investigation by 0.74 percent.

VIII. SUMMARY

The results of the present investigation confirm the suspected existence of exceedingly large uncertainties in the hitherto existing "best" values for the heats of combustion of ethane, propane, normal butane, and normal pentane. The values from the previous investigations given in the preceding section of the present paper were computed from the original data by this writer; while the values which have mostly been used for the heats of combustion of these gases are those given in the International Critical Tables (11). These latter values were taken from the compilation by Kharasch (12), and, when corrected to a temperature of 25 C, are all lower than those from the present investigation by the following respective amounts: Ethane, 1.23 percent; propane, 0.87 percent; normal butane, no existing data; normal pentane, 0.86 percent. These differences are from 30 to 50 times the estimated uncertainties in the values obtained from the present investigation.

The data of the present investigation give, for the heat involved in the reaction, C_nH_{2n+2} (gas) $+\frac{3n+1}{2}O_2$ (gas) $= nCO_2$ (gas) $+ (n+1)H_2O$ (liquid) at a temperature of 25 C and a constant total pressure of 1 atmosphere, the following values for ethane, propane, normal butane, and normal pentane:

TABLE 10.—*Results of the present investigation*

Substance	Formula	State	Heat of combustion[a] at 25 degrees C and a constant pressure of 1 atmosphere	
			International kilojoules per mole (fundamental unit)	$k\text{-}cal_{15}$ per mole (defined unit)
Ethane	C_2H_6	Gas	1559.57±0.44	372.81±0.11
Propane	C_3H_8	Gas	2219.57± .51	530.57± .12
Normal butane	$n\text{-}C_4H_{10}$	Gas	2877.88± .63	687.94± .15
Normal pentane	$n\text{-}C_5H_{12}$	Gas	3536.00± .88	845.27± .21

[a] As explained in sec. II, p. 736, the fundamental unit of energy in the present investigation is the international joule based upon standards maintained at this Bureau, while the $k\text{-}cal_{15}$ is a defined unit, 1 $k\text{-}cal_{15}$ being taken equivalent to 4.1850/1.00040 international kilojoules. One mole (18.0156 g, true mass) of H_2O is taken as equivalent to ⅔ mole of C_2H_6, to ¼ mole of C_3H_8, to ⅕ mole of C_4H_{10}, and to ⅙ mole of C_5H_{12}.

Data have now been obtained in this laboratory on the heats of combustion of all the normal paraffin hydrocarbons in the gaseous state from methane to pentane, inclusive. In a subsequent paper, these data will be utilized: First, in the calculation of the heats of formation of these molecules; second, in the accurate prediction of the heats of combustion and of formation of the gaseous normal paraffin hydrocarbons containing more than five carbon atoms in the molecule; and third, in drawing conclusions concerning the energies of the atomic linkages in these molecules.

The author is deeply grateful to the late Dr. Edward W. Washburn for his helpful advice, his many valued suggestions, and his keen interest in this work.

IX. REFERENCES

1. Thomsen, J., Thermochemische Untersuchungen, vol. IV, pp. 50–54. Barth Leipzig, 1886.
2. Berthelot, M., and Matignon, C., Ann. chim. phys., vol. 30, p. 547, 1893.
3. Roth, W. A., and Machlett, unpublished. The numerical result appears in the Landolt-Börnstein-Roth-Scheel Tabellen, 5th ed., vol. II, p. 1588. Springer, Berlin, 1923.
4. Vinal, G. W., B.S.Jour. Research, vol. 8, p. 448, 1932.
5. Baxter, G. P., Curie, M., Hönigschmid, O., LeBeau, P., and Meyer, R. J., J. Am. Chem. Soc., vol. 56, p. 753, 1934.
6. Rossini, F. D., B.S.Jour. Research, vol. 6, pp. 1, 37, 1931; vol. 7, p. 329, 1931; vol. 8, p. 119, 1932; vol. 9, p. 679, 1932.
7. Shepherd, M., B.S.Jour. Research, vol. 12, p. 185, 1934.
8. Mair, B. J., B.S.Jour. Research, vol. 9, p. 457, 1932.
9. Griffiths, E., and Awbery, J. H., Engineering, vol. 133, p. 84, 1932.
10. International Critical Tables, vol. 3, p. 220. McGraw-Hill Book Company, New York, 1928.
11. Ibid., vol. 5, p. 163.
12. Kharasch, M. S., B.S.Jour. Research, vol. 2, p. 359, 1929.
13. Curtis, H. L., and Curtis, R. W., B.S.Jour. Research, vol. 12, p. 665, 1934.

WASHINGTON, March 15, 1934.

U.S. DEPARTMENT OF COMMERCE BUREAU OF STANDARDS

RESEARCH PAPER RP687

Part of Bureau of Standards Journal of Research, vol. 12, June 1934

STUDY OF THE SYSTEM CaO–SiO_2–H_2O AT 30 C AND OF THE REACTION OF WATER ON THE ANHYDROUS CALCIUM SILICATES

By E. P. Flint and Lansing S. Wells

ABSTRACT

A graph has been prepared representing the solubility of silica at 30 C in solutions containing increasing concentrations of lime up to saturation, the solutions being in "equilibrium" with solid phases composed of hydrated combinations of lime and silica. An electrometric and analytical study of both supersaturated and unsaturated solutions of silica at definite concentrations of lime, when correlated with these equilibrium solubility relationships, indicates the existence of definite compounds in the system CaO–SiO_2–H_2O which may be the hydrated calcium salts of orthosilicic acid. Experimental values were obtained for the hydrolysis constants of these salts from which ionization constants for the four steps in the dissociation of orthosilicic acid were calculated. A study of the reaction of water upon the anhydrous calcium silicates ($CaO \cdot SiO_2$, $3CaO \cdot 2SiO_2$, γ–$2CaO \cdot SiO_2$, β–$2CaO \cdot SiO_2$, $3CaO \cdot SiO_2$) showed that the products formed depend upon the equilibrium relationships of the system CaO–SiO_2–H_2O. Of these compounds all but monocalcium silicate ($CaO \cdot SiO_2$) form solutions which precipitate hydrated calcium silicate on standing. Application of the same methods to a study of the reaction of water upon a portland cement indicated that hydrated calcium orthosilicate is formed during the hydration of portland cement. A study of the reaction between diatomaceous silica and lime solution and between silica gel and lime solution is also included.

CONTENTS

	Page
I. Introduction	752
II. Preliminary study of the system CaO–SiO_2–H_2O at 30 C	753
1. Preparation of materials	753
2. Method of procedure	753
3. Discussion of results	754
III. Constitution of calcium silicate solutions	757
1. The combination of lime and silica in calcium silicate solutions	757
2. Equations for the successive stages in the hydrolysis of calcium orthosilicate	760
3. Hydrolysis of $Ca(H_3SiO_4)_2$	761
4. Hydrolysis of CaH_2SiO_4	763
5. Hydrolysis of $Ca_3(HSiO_4)_2$	765
6. Hydrolysis of Ca_2SiO_4	766
7. The ionization constants of orthosilicic acid	766
8. Discussion of results with reference to solubility relationships in the system CaO–SiO_2–H_2O	768
IV. Reaction of water on the anhydrous calcium silicates	771
1. Method of procedure	771
2. Reaction of water on monocalcium silicate ($CaO \cdot SiO_2$)	771
3. Reaction of water on tricalcium disilicate ($3CaO \cdot 2SiO_2$)	773
4. Reaction of water on gamma-dicalcium silicate (γ–$2CaO \cdot SiO_2$)	773
5. Reaction of water on beta-dicalcium silicate (β–$2CaO \cdot SiO_2$)	774
6. Reaction of water on tricalcium silicate ($3CaO \cdot SiO_2$)	775
7. Reaction of water on portland cement	776
V. Reactions of diatomaceous silica and of silica gel with lime solution	780
VI. Summary	782

I. INTRODUCTION

An experimental study of the system lime-silica-water should possess considerable practical value not only for its direct bearing upon the problem of the setting of portland cement and hydraulic mortars but also for possible applications in fields of geology, soil equilibria, and water purification. In this report the relationship of the system to products formed by the reaction of portland cement with water will be especially considered.

Unfortunately it proved impossible to utilize petrographic methods in this study, owing to the apparently amorphous character of the solid phases formed by reactions between lime, silica, and water at room temperature. Hence the evidence obtained for the existence of definite compounds in the solid phases is indirect. Although it is realized that the state of combination of lime and silica in solution does not necessarily bear a direct relation to that in the solid phase, yet often changes which occur in the aqueous phase are of aid in interpreting changes which may take place in the solid phase. Accordingly, an investigation was made of the composition of lime-silica solutions to obtain as much indirect evidence as possible as to the probable composition of the solid phases with which these solutions might exist in equilibrium.

The term equilibrium will be used for the purpose of this paper to designate an apparently steady state between solid phase and solution, the composition of neither undergoing appreciable change in time periods of from several weeks to several months. It is recognized that this equilibrium may be displaced by the eventual crystallization of the solid phase, a process which, however, appears to proceed exceedingly slowly at room temperature.

The first part of this paper deals with the solubility relationships of lime and silica, and presents correlations between the compositions of hydrated solid phases and of solutions with which they may exist in equilibrium, and with the state of combination of lime and silica in these solutions as determined electrometrically.

The paper next considers the reaction of water upon compounds occurring in the binary system, lime-silica, in the light of the foregoing study. These compounds have the following molecular proportions:[1] $CaO{\cdot}SiO_2$, $3CaO{\cdot}2SiO_2$, $2CaO{\cdot}SiO_2$, and $3CaO{\cdot}SiO_2$. Tricalcium silicate ($3CaO{\cdot}SiO_2$) and dicalcium silicate in its beta modification (β–$2CaO{\cdot}SiO_2$) are the major constituents of portland cement,[2] in which the gamma form of dicalcium silicate (γ–$2CaO{\cdot}SiO_2$) also appears occasionally. It will be shown that the generalization of Le Chatelier [3] that hydraulic materials possess metastable solubilities, applies to the calcium silicates occurring in portland cement.

Finally the reactions of diatomaceous silica and of silica gel with lime in solution are compared and the relationship of the results to the system CaO–SiO_2–H_2O is discussed briefly.

[1] A. L. Day, E. S. Shepherd, and F. E. Wright, The lime-silica series of minerals, Am. Jour. Sci., series 4 vol. 22, p. 265, 1906.

[2] G. A. Rankin, A study of the constitution of portland cement clinker, Jour. Ind. Eng. Chem., vol. 3, pp. 211–227, 1911; P. H. Bates, The constitution of portland cement, Concrete and Cement Age (Cement Mill Section) vol. 2, pp. 3–4, 1913; G. A. Rankin and F. E. Wright, The ternary system CaO–Al_2O_3–SiO_2, Am. Jour. Sci., series 4, vol. 39, pp. 1–79, 1915.

[3] H. Le Chatelier, Recherches Expérimentales sur la Constitution des Mortiers Hydrauliques, Thése, Paris, 1887. Englisn translation also prepared by J. L. Mack, New York, 1905.

II. PRELIMINARY STUDY OF THE SYSTEM CaO–SiO_2–H_2O AT 30 C

1. PREPARATION OF MATERIALS

Colloidal silica gel is probably the most reactive form of silica, but is difficult to prepare in the pure state. In this study, commercial granular silica gel, ground to pass a no. 200 sieve, and purified according to the method of Bennett,[4] was used. This method of purification involved boiling with concentrated nitric acid followed by repeated washing and subsequent electrolysis in distilled water with continuous removal of the solution at the electrodes. No nitric acid could be detected by qualitative tests in silica purified by the above method and used in this investigation. It had a nonvolatile residue of 0.02 percent, based on the weight of the ignited silica.

Distilled water for the solutions was freed from carbon dioxide by boiling and subsequently cooling in a stream of CO_2-free air. The preparation of calcium hydroxide solutions has been described previously.[5]

2. METHOD OF PROCEDURE

Preliminary experiments showed that silica gel dissolves slowly in dilute calcium hydroxide solutions at 30 C, but that increase of temperature had a marked effect upon its solubility and rate of solution. Thus, boiling an excess of purified silica gel with dilute solutions of calcium hydroxide for several days produced solutions generally containing 0.4 to 0.5 g SiO_2 and 0.02 to 0.05 g of CaO per liter. Although these solutions were perfectly clear on filtering at the boiling point, they gradually assumed a light-blue color on cooling to room temperature. Evidently this is due to a decreased solubility of silica at the lower temperature which results in the separation of a portion of the silica in the form of a colloidal sol. Such sols are very stable and may stand for months at room temperature with only very slight alteration in composition or appearance.

However, it was found that precipitation of the colloidal silica could be effected quite readily by the addition of a small quantity of saturated calcium hydroxide solution. The precipitated silica was then easily removed by filtration. Although the initial sol-containing solutions when examined under the ultra microscope were seen to contain myriads of particles in Brownian movement, no trace of such movement could be detected in the clear solutions after precipitation. It was assumed, therefore, that the latter were true solutions saturated with respect to silica at definite concentrations of calcium hydroxide.

To investigate further the solubility relationships of silica and lime, a large quantity of the sol-containing solution was prepared, care being taken to avoid contamination by carbon dioxide of the air. The composition of this solution corresponds to point A in figure 1.

This solution was then mixed in various proportions with a calcium hydroxide solution of the composition represented by point B, figure 1. Great care was taken to measure out the volume of these solutions accurately and to exclude CO_2 so that the initial compositions of the

[4] Personal communication from Prof. E. Emmet Reid.

[5] E. P. Flint and Lansing S. Wells, The activity coefficients of hydroxyl ion in solutions of calcium hydroxide at 30 C, B. S. Jour. Research, vol. 11 (RP584), pp. 163–171, 1933.

resultant mixtures, represented by points on the diagonal AB, might be accurately known.

The mixtures, in well-stoppered flasks, were placed directly in an air thermostat [6] maintained at $30 \pm 0.05°$ C. Rapid separation of a part of the lime and silica in the form of voluminous flocculent precipitates occurred as the solutions changed from unstable states to conditions more nearly approaching equilibrium. After 1 month the solutions were filtered from the precipitates and were analyzed for silica and lime, using 400 to 700 ml samples. Silica was determined by double dehydration, ignition to constant weight followed by volatilization with hydrofluoric acid and reignition to constant weight. Lime was precipitated as calcium oxalate and ignited to constant weight as the oxide. All evaporations and ignitions were made in platinum.

The proportions of lime to silica in the precipitates were obtained from the differences between the compositions of the solutions before and after precipitation. This method seemed preferable to direct analysis of the solid phases due to the difficulty of obtaining representative samples of these precipitated materials, part of which adhered quite firmly to the interiors of the flasks. It also avoids uncertainties involved in the washing of these bulky precipitates with alcohol and ether which may further precipitate lime and silica from the mother liquor retained after filtration and thus alter their composition. Control experiments showed that no appreciable quantity of lime was taken up by tne glass in the time period used.

3. DISCUSSION OF RESULTS

The results are illustrated by figure 1, where the curve CDEFB represents the solubility of silica in solutions containing increasing concentrations of lime. The initial compositions of the unstable lime-silica solutions are represented by points on the diagonal AB. Broken lines from these points to points on the curve CDEFB connect the initial and final compositions. The figures accompanying these lines give the molar ratios of lime to silica in the precipitated material calculated from the differences between the initial and final compositions of the solutions.

The concentration of silica in the clear saturated solutions at first rises sharply from C to a maximum at D and then decreases as the concentration of lime increases. At the point E the direction of the solubility curve changes. From E the concentration of lime diminishes to a minimum at F where there is again a change in the direction of the solubility curve. Subsequently, as the concentration of lime increases from its minimum value at F to the value at B, the amount of silica in solution decreases to very low values.

Table 1 contains part of the data from which figure 1 was constructed.

[6] For description see Lansing S. Wells, Reaction of Water on Calcium Aluminates, B.S. Jour. Research, vol. 1 (RP34), p. 954, 1928.

TABLE 1.—*Compositions of equilibrium solutions and molar ratios of lime to silica in precipitates which separated from unstable lime-silica solutions of initial compositions lying on AB in figure 1*

1	2	3	4	5	1	2	3	4	5
Number	Composition of solutions		Molar ratio of CaO/SiO_2		Number	Composition of solutions		Molar ratio of CaO/SiO_2	
	CaO	SiO_2	In solution	In precipitate		CaO	SiO_2	In solution	In precipitate
	g/l	g/l				g/l	g/l		
1	0.0273	0.1771	[a] 0.17	0.040	8	.0943	.2208	.48	.422
2	.0304	.1836	.18	.049	9	.1015	.2062	[c] .53	.537
3	.0380	.2340	.17	--------	10	.0741	.1639	.46	.930
4	.0431	.2790	.17	.061	11	.0590	.1198	.53	.997
5	.0702	.3260	[b] .23	.103	12	.0482	.0760	[d] .68	1.03
6	.0852	.3068	.30	.217	13	.0493	.0465	1.14	1.07
7	.0954	.2610	.39	.293					

[a] C, fig. 1. [b] D, fig. 1. [c] E, fig. 1. [d] F, fig. 1.

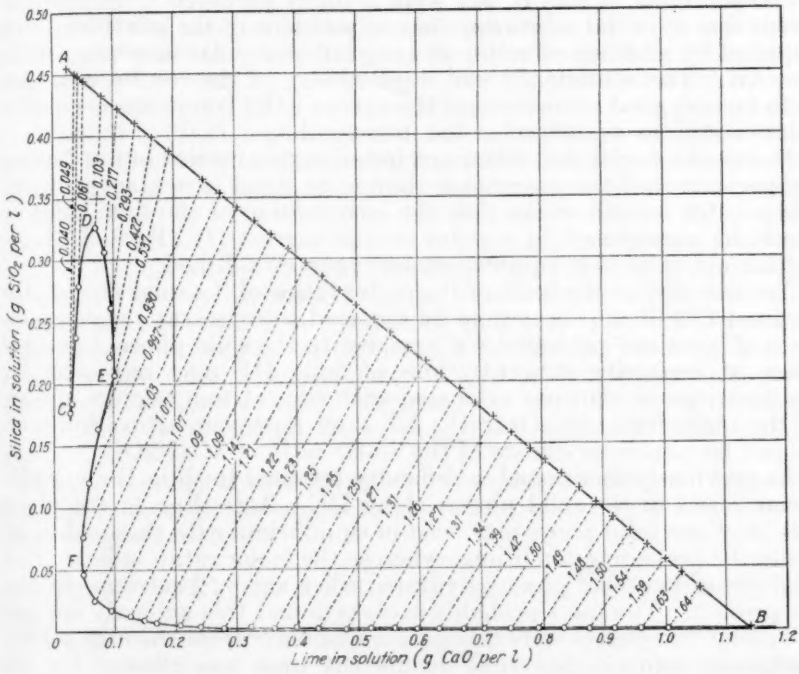

FIGURE 1.—*Showing the quantity of silica at 30 C in solutions of increasing lime concentration which are saturated with respect to hydrated solid phases containing lime and silica in the molar proportions shown.*

It will be shown later by an electrometric method that of the total lime in solution in the region of the curve CDEF a relatively small proportion is uncombined and that the molar ratios in column 4 very nearly represent the actual state of combination in solution. Thus, molar ratios between 0 and 0.5 may represent equilibria between hydrated silica and a calcium silicate containing lime and silica in the

molar proportion $1CaO:2SiO_2$. Molar ratios between 0.5 and 1 may represent equilibria between two calcium silicates of molar proportions $1CaO:2SiO_2$ and $1CaO:1SiO_2$. This possibility will be considered in detail in the following section.

The solid phases in equilibrium with solutions along the curve CD contain only a few hundredths of a mol of lime per mol of silica (table 1, column 5) and may consist, therefore, of hydrated silica with a small amount of adsorbed lime. Along the curve EF the molar ratio of lime to silica in the solid phases is unity within the experimental accuracy. In the intermediate region along DE the molar ratios vary between 0.2 and 0.5, but for reasons which will become apparent, it is believed that the true molar ratio in this region may be 0.5. To verify this supposition two additional compositions were prepared in the vicinity of solutions nos. 6 and 7 of table 1 and these precipitated materials of CaO/SiO_2 molar ratios of 0.39 and 0.48, respectively, in somewhat better agreement with the theory.

It should be noted here that the initial compositions along the diagonal AB were not all prepared at the same time nor from the same initial solutions, A and B, but were actually prepared from four different sets of initial solutions, the compositions of the mixtures being adjusted by addition of water so as to fall at regular intervals on the line AB. The consistency and duplicability of the results was such as to furnish good evidence that the curve CDEFB represents equilibrium conditions as defined in the introduction.

It was also found that when precipitation was carried out at boiling temperature and the precipitate allowed to stand in contact with the solution for several weeks that the composition of the final solution would be represented by a point on the curve CDEFB, thus giving further evidence that equilibrium had been established.

Tentatively, on the basis of the molar ratios of the solid phases, the segment CD of the curve may be assumed to represent the compositions of solutions saturated with respect to the solid phase, hydrated silica, at increasing concentrations of lime; DE may represent the compositions of solutions saturated with respect to a calcium silicate of the molar ratio $1CaO:2SiO_2$; EF may represent saturation with respect to a calcium silicate of the molar ratio $1CaO:1SiO_2$.

As previously mentioned, a difficulty presents itself in the variable molar ratios in the solid phases along DE. According to the phase rule only one solid phase may exist in equilibrium with these solutions under the prevailing conditions, whereas the molar ratios indicate that mixtures of two solid phases, hydrated silica and 1:2 calcium silicate, are present. The most probable explanation of this anomaly appears to be that two phases were precipitated together from the original sol-containing solution and that insufficient time was allowed for the system to approach a steady state which would have resulted in the transformation of the hydrated silica into calcium silicate. Experiments showed that re-solution of precipitates consisting of hydrated silica does not readily take place even at boiling temperature, hence it is to be expected that the reaction of solid hydrated silica with lime in solution to give solid calcium silicate would be a slow process. It is therefore believed that the curve DE represents the compositions of solutions saturated with respect to the 1:2 calcium silicate, although the steady state previously defined as equilibrium in the solid phase had not been attained.

The highest molar ratio of lime to silica in the solid phase indicated in figure 1 is 1.64. When a small volume of silica solution was mixed with a large volume of saturated lime solution, precipitates containing higher molar ratios of lime to silica were obtained. They were filtered off, washed with alcohol and ether, and analyzed. At lime concentrations of 1.052 and 1.159 g of CaO per liter, the molar ratios of lime to silica in the precipitates were 1.79 and 1.85, respectively. Thus it appears that the molar ratio $2CaO:1SiO_2$ is approached when the solid phase is in equilibrium with saturated lime solution.

These hydrated calcium silicate precipitates were found to set to a hard mass after drying between filter paper and in a desiccator. A similar observation has been made by Michaelis [7] and forms the basis of his "inner desiccation" theory for the hardening of portland cement. The mechanism of the formation of precipitates of entirely similar properties from metastable solutions of the anhydrous calcium silicates will be considered later in this paper. It will be shown there that Le Chatelier's theory of the metastable solubility of hydraulic materials is a necessary complement of Michaelis' theory of hydraulic hardening.

A number of previous investigators have prepared hydrated calcium silicates to which they have assigned formulas on the basis of analytical evidence. Le Chatelier,[8] from experiments on the reaction between hydrated silica and lime solution, concluded that the composition $CaO{\cdot}SiO_2{\cdot}2\ 1/2H_2O$ represents a definite compound and that higher molar ratios of lime to silica result from the adsorption of lime by this compound. Jordis and Kanter,[9] by similar means, obtained a product corresponding in composition to the formula $CaO{\cdot}SiO_2{\cdot}H_2O$. Klassee [10] likewise prepared a hydrated calcium silicate having the molar ratio $CaO/SiO_2=1$ by the reaction: $Na_2SiO_3+Ca(NO_3)_2\rightarrow 2NaNO_3+CaSiO_3$. He also obtained a hydrated silicate in which the molar proportion CaO/SiO_2 was equivalent to 3:2 by substituting sodium orthosilicate for sodium metasilicate. On shaking the resulting calcium silicate with saturated calcium hydroxide solution, the molar proportion of lime to silica increased to 1.8. From these experiments Klassee postulated the existence of hydrated 1:1, 3:2, and 2:1 calcium silicates.

Also, a number of crystalline hydrated calcium silicates containing lime and silica in the molar ratios, 1:2, 1:1, 3:2, and 2:1, occur in nature as rare minerals.[11]

III. CONSTITUTION OF CALCIUM SILICATE SOLUTIONS

1. THE COMBINATION OF LIME AND SILICA IN CALCIUM SILICATE SOLUTIONS

This portion of the investigation deals with a study of the equilibria existing in lime-silica solutions and the bearing of these equilibria upon the composition of solid phases which occur in the system CaO–SiO_2–H_2O. The assumption is made throughout that silica can exist in solution as a definite crystalloidal silicic acid capable of

[7] W. Michaelis, Recognition of Hydraulic Cements, Prot. Ver. D.P.C.F., 1909.
[8] See footnote 3, p. 752.
[9] E. Jordis and E. H. Kanter, Contributions to the Knowledge of the Silicates, I, Z. anorg. Chem., vol. 35, p. 82, 1903.
[10] F. Klassee, Attempts to Prepare Calcium Hydrosilicates, Zement, vol. 17, p. 48, 1928.
[11] V. A. Vigfusson, The Hydrated Calcium Silicates, Am. Jour. Sci., vol. 21, pp. 67–78, 1931.

forming salts with calcium hydroxide. Justification for this view is furnished not only by the consistent interpretation which it gives to the observed data, but also by the work of previous investigators, including: (a) The construction of titration curves characteristic of a weak acid and the derivation of ionization constants therefrom,[12] (b) molecular weight determinations by freezing point lowering,[13] (c) preparation of organic derivatives of silicic acid such as ethyl orthosilicate,[14] (d) the crystallization of definite silicates from solution,[15] (e) measurements of conductivity of silicate solutions which indicate the presence of definite compounds therein,[16] (f) assignment of transference numbers to silicate ions,[17] and (g) diffusion experiments.[18]

As all lime-silica solutions prepared in this study were alkaline it was assumed that they contained mixtures of calcium hydroxide and calcium silicate formed by the partial or complete neutralization of silicic acid. The extent of combination between lime and silica in such silicate solutions was determined by electrometric measurements upon the cells:

$$\left.\begin{array}{l}(1)\ \mathrm{H_2}\,|\,\mathrm{Ca(OH)_2(c)}\,|\,\mathrm{KCl\ (saturated)}\,|\,\mathrm{HgCl+Hg}\\ (2)\ \mathrm{H_2}\,\left|\begin{array}{l}\mathrm{Ca(OH)_2(c)}\\ \mathrm{Ca\ silicate}\end{array}\right|\,\mathrm{KCl\ (saturated)}\,|\,\mathrm{HgCl+Hg}\end{array}\right\}\text{at 30 C.}$$

The type of hydrogen electrodes and calomel half cell used and other details have been reported previously.[19]

The potentials of cells (1) and (2) should be identical when the concentration, $Ca(OH)_2(c)$, in the two cells is the same, assuming that the alteration of the potential of the liquid junction, $Ca(OH)_2$ (c) | KCl (saturated), caused by the presence of calcium silicate, is negligible. With cell (1) the relationship between potential and calcium hydroxide concentration may be determined by direct measurements. Knowing this relationship the concentration of uncombined calcium hydroxide in calcium silicate solutions may readily be obtained from electrometric measurements. The difference between the total dissolved lime and that present as uncombined calcium hydroxide must represent lime combined as calcium silicate.

To determine the concentration of uncombined calcium hydroxide corresponding to a given electromotive force, measurements of the potentials of cell (1) were made for various concentrations of calcium hydroxide. Table 2 gives the data obtained. The pH values given in this and subsequent tables were calculated from a formula used in a previous electrometric study of solutions derived from the calcium

[12] A. F. Joseph and H. B. Oakley, The Action of Silica on Electrolytes, Jour. Chem. Soc., vol. 127, pp. 2813–2818, 1925; H.T.S. Britton, Electrometric Study of the Precipitation of Silicates, Jour. Chem. Soc., pp. 425–436, 1927; R. W. Harman, Aqueous Solutions of Sodium Silicates, VII, Jour. Phys. Chem., vol. 31, pp. 616–625, 1925; W. D. Treadwell and W. Wieland, The Hydrates of Silicic Acid, Helv. Chim. Acta, vol. 13, pp. 842–864, 1930.

[13] R. Willstätter, H. Kraut, and K. Lobinger, The Simplest Silicic Acids, Ber., 61B, pp. 2280–2293, 1928.

[14] A. W. Dearing and E. E. Reid, Alkyl Orthosilicates, Jour. Am. Chem. Soc., vol. 50, pp. 3058–3062, 1928.

[15] K. A. Vesterberg, $Na_2SiO_3{\cdot}9H_2O$, A Well-Defined Crystalline Sodium Silicate, Zs. anorg. Chem., vol. 88, 341–348, 1914; G. W. Morey, New Crystalline Silicates of Potassium and Sodium, Their Preparation and General Properties, Jour. Am. Chem. Soc., vol. 36, pp. 215–230, 1914.

[16] F. Kohlrausch, Solutions of Sodium Silicates, Zs. Physik. Chem., vol. 12, pp. 773–791, 1893; R. W. Harman, Aqueous Solutions of the Sodium Silicates, I, Jour. Phys. Chem., vol. 29, pp. 1155–1168, 1925.

[17] R. W. Harman, Aqueous Solutions of the Sodium Silicates, II, Jour. Phys. Chem., vol. 30, pp. 359–368, 1926.

[18] P. B. Ganguly, Diffusion of Aqueous Sodium Silicate Solutions Across Semipermeable Membranes, Jour. Phys. Chem., vol. 31, pp. 407–416, 1927.

[19] See footnote 5, p. 753.

aluminates, $pH = \frac{\text{emf (observed)} - 0.2437}{0.06011}$, in order to preserve uniformity with that investigation.[20] This formula neglects liquid junction potentials and the values of pH are inserted merely for comparative purposes and to indicate the range covered.

TABLE 2.—*Electromotive force measurements upon the cell,* $H_2|Ca(OH)_2(c)|KCl$ *(saturated)*$|HgCl+Hg$ *at 30 C, and the* pH *of calcium hydroxide solutions calculated therefrom*

1	2	3	4	1	2	3	4
No.	$Ca(OH)_2$ concentration	emf	pH[a]	No.	$Ca(OH)_2$ concentration	emf	pH[a]
	g CaO/l	*v*			*g CaO/l*	*v*	
1	0.00083	0.78896	9.07	11	0.4002	0.95582	11.85
2	.00169	.81446	9.50	12	.4987	.96106	11.94
3	.00314	.83278	9.80	13	.5983	.96502	12.00
4	.00631	.85156	10.11	14	.6988	.9686	12.06
5	.0124	.87102	10.44	15	.8004	.9720	12.12
6	.0248	.88796	10.72	16	.8997	.9745	12.16
7	.0500	.90621	11.02	17	.9995	.97677	12.20
8	.1024	.92346	11.31	18	1.092	.9790	12.23
9	.2004	.93925	11.57	19	1.199	.9810	12.26
10	.2980	.94888	11.73				

[a] Calculated from relationship, $pH = \frac{\text{emf (observed)} - 0.2437}{0.06011}$.

In correlating data obtained by measurements upon cells of type (2) it was first assumed that lime and silica were combined in solution as monocalcium silicate (the calcium salt of metasilicic acid) and that only the calcium hydroxide in excess of this compound contributed to the potential of the cell. Figure 2 compares potential measurements made upon cell (1) with potential measurements made upon cell (2) for solutions derived from various sources and containing varying amounts of lime and silica and in which the lime present as calcium hydroxide is computed as that in excess of monocalcium silicate. A portion of the data for calcium silicate solutions contained in this figure will be presented in subsequent tables.

Inspection of figure 2 shows that if only a small amount of lime is present in excess of that required to form monocalcium silicate the emf of cell (2) is greater than that corresponding to the excess lime. Hence less lime must be combined with silica than is required by the molar ratio $1CaO:1SiO_2$. At higher concentrations of lime in excess of $CaO \cdot SiO_2$ the relationship is more closely fulfilled. With increasing concentration of calcium hydroxide the emf of cell (2) is less than that corresponding to lime in excess of monocalcium silicate, hence more lime must be combined with silica than corresponds to the ratio $1CaO:1SiO_2$.

A survey of the compositions of these calcium silicate solutions and of the emf data showed that: (1) Lime and silica in solution may be combined in a molar ratio of less than $1CaO:1SiO_2$, when the concentration of lime is low and that of silica relatively high; (2) the molar ratio of combined lime to silica may be greater than $1CaO:1SiO_2$ when the concentration of lime is high compared to the concentration

[20] See footnote 6, p. 754.

of silica; (3) the molar ratio may equal $1CaO:1SiO_2$ in an intermediate region. It was shown in the previous section that the solid phases which precipitate from such solutions or are in equilibrium with them increase in lime content from a molar ratio of $0.04CaO:1SiO_2$ at the lowest lime concentration studied (0.0273 g CaO per l) to a molar ratio approaching $2CaO:1SiO_2$ when in contact with saturated lime solution.

Consideration of these facts led to the assumption that the calcium silicates present in the system $CaO-SiO_2-H_2O$ at 30 C are salts not of metasilicic acid but of orthosilicic acid (H_4SiO_4) of which four are possible: $Ca(H_3SiO_4)_2$, CaH_2SiO_4, $Ca_3(HSiO_4)_2$, and Ca_2SiO_4, in which the molar ratios of lime to silica are 1:2, 1:1, 3:2, and 2:1.

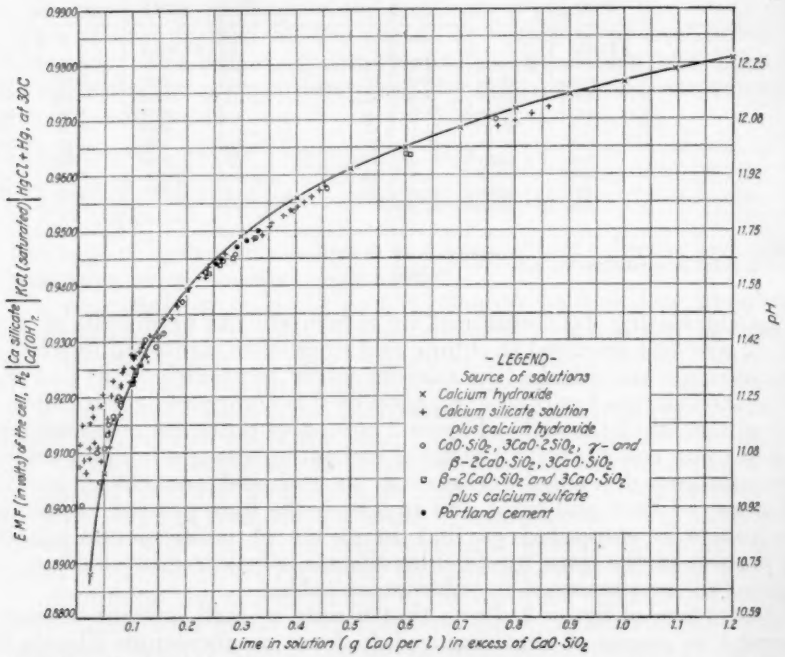

FIGURE 2.—*Correlation of electrometric measurements upon calcium hydroxide and calcium silicate solutions indicating that silica is not combined as monocalcium silicate at all concentrations of lime.*

2. EQUATIONS FOR THE SUCCESSIVE STAGES IN THE HYDROLYSIS OF CALCIUM ORTHOSILICATE

The hydrolyses of these calcium silicates and the corresponding mass action equilibrium expressions, assuming complete dissociation of calcium hydroxide and of the calcium silicates involved, are represented by the following equations:

$$Ca(H_3SiO_4)_2 + 2H_2O \rightleftharpoons 2H_4SiO_4 + Ca(OH)_2 \tag{1}$$

$$K_{h_1} = \frac{[H_4SiO_4]\,[OH^-]}{[H_3SiO_4^-]} \tag{1a}$$

$$2CaH_2SiO_4 + 2H_2O \rightleftharpoons Ca(H_3SiO_4)_2 + Ca(OH)_2 \tag{2}$$

$$K_{h_3} = \frac{[H_3SiO_4^-]\,[OH^-]}{[H_2SiO_4^{=}]} \tag{2a}$$

$$Ca_3(HSiO_4)_2 + 2H_2O \rightleftharpoons 2CaH_2SiO_4 + Ca(OH)_2 \tag{3}$$

$$K_{h_2} = \frac{[H_2SiO_4^{=}]\,[OH^-]}{[HSiO_4^{\equiv}]} \tag{3a}$$

$$2Ca_2SiO_4 + 2H_2O \rightleftharpoons Ca_3(HSiO_4)_2 + Ca(OH)_2 \tag{4}$$

$$K_{h_1} = \frac{[HSiO_4^{\equiv}]\,[OH^-]}{[SiO_4^{\equiv}]} \tag{4a}$$

K_{h_1}, K_{h_2}, K_{h_3}, and K_{h_4} are the equilibrium constants for the successive stages in the hydrolysis of calcium orthosilicate, Ca_2SiO_4.

Relationships between these hydrolysis constants and the ionization constants of orthosilicic acid will be developed later.

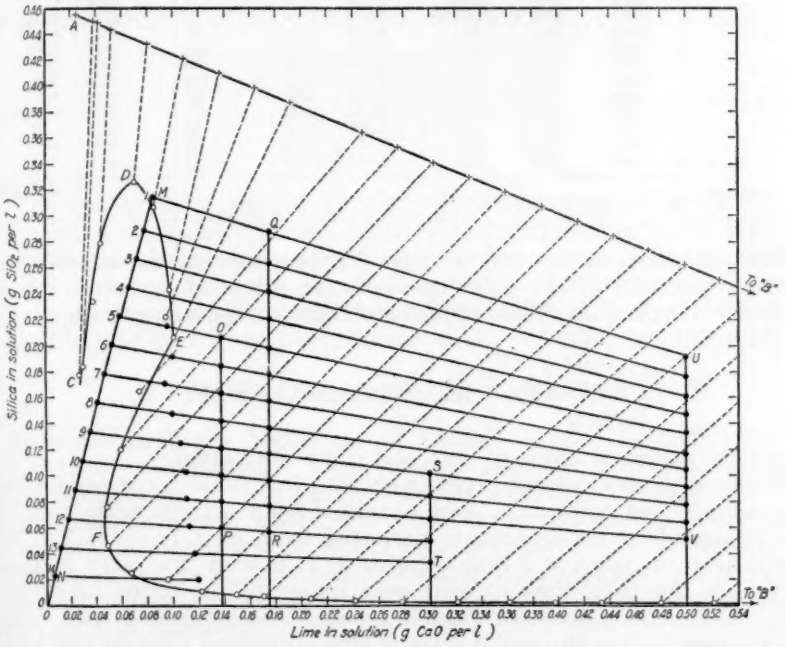

FIGURE 3.—*Showing the compositions of series of solutions prepared for investigation of the state of combination of lime and silica in solution at various lime concentrations and the relationships of these compositions to the diagram of figure 1.*

3. HYDROLYSIS OF $Ca(H_3SiO_4)_2$

The validity of equation 1a, the mass action expression for the hydrolysis of the least basic calcium silicate, $Ca(H_3SiO_4)_2$, in its application to calcium silicate solutions was first investigated. For this purpose a series of dilutions of a silica solution, prepared according to the method described in the previous section, was made up. Their compositions are given in columns 2 and 3 of table 3 and are represented by points along the line MN of figure 3. Actually 2 series of dilutions of 2 different solutions were prepared, the first 4 composi-

tions of table 3 belonging to 1 group, and the remainder to another. The stable phase in contact with solutions of these compositions was found in the previous section to be probably hydrated silica.

TABLE 3.—*Data used in determining the hydrolysis constant K_{h_4} of the reaction:* $Ca(H_3SiO_4)_2+2H_2O\rightleftharpoons 2H_4SiO_4+Ca(OH)_2$

1	2	3	4	5	6	7	8	9
No.	Composition of solutions		emf of cell	CaO corresponding to emf	pH	Molar ratio of combined CaO to total SiO_2 in solution	SiO_2 in excess of Ca $(H_3SiO_4)_2$	$K_{h_4}\times 10^4$
	CaO	SiO_2						
	g/l	*g/l*	*v*	*g/l*			*g/l*	
1	0.0846	0.3136	0.82872	0.00267	9.73	0.280	0.1324	7.44
2	.0780	.2890	.82823	.00264	9.72	.279	.1219	7.44
3	.0720	.2668	.82802	.00261	9.72	.279	.1126	7.40
4	.0660	.2446	.82766	.00259	9.72	.278	.1064	6.86
5	.0584	.2226	.8241	.00229	9.66	.270	.0975	6.96
6	.0526	.2003	.8229	.00222	9.64	.269	.0876	6.78
7	.0467	.1781	.8219	.00215	9.62	.268	.0781	6.82
8	.0409	.1558	.8203	.00202	9.59	.266	.0682	6.27
9	.0350	.1336	.8202	.00201	9.59	.264	.0586	6.39
10	.0292	.1113	.8191	.00196	9.57	.262	.0488	6.51
11	.0234	.0890	.8189	.00195	9.57	.258	.0389	6.52
12	.0175	.0668	.8183	.00191	9.56	.250	.0293	6.81
13	.0116	.0445	.8147	.00171	9.50	.238	.0197	6.73
14	.0058	.0223	.8079	.00138	9.39	.213	.0099	6.68
Average								6.8×10^{-4}

The potentials of the cell of type (2) were measured immediately after preparation of the solutions and are recorded in column 4 of table 3. If equation (1) is applicable these measurements are given by the cell:

$$H_2 \left| \begin{matrix} Ca(OH)_2 \\ Ca(H_3SiO_4)_2 \\ H_4SiO_4 \end{matrix} \right| KCl \text{ (saturated)} \mid HgCl+Hg,$$

where the concentrations of lime and silica are varied.

The lime concentrations given in column 5 of table 3, corresponding to the measured potentials, were obtained from a large scale plot of emf against lime concentration prepared from data in table 2. By comparison of columns 2 and 5 (table 3) it is seen that only a small portion of the total lime present contributes to the potential of the cell. That which does nor contribute must be combined with silica and column 7 gives the molar ratio of this combined lime to the total silica. Evidently if equation (1) represents the equilibrium existing in these solutions this molar ratio should be intermediate between $CaO/SiO_2=0.5$, corresponding to the compound $Ca(H_3SiO_4)_2$, and $CaO/SiO_2=0$, corresponding to H_4SiO_4. It is seen that this condition is fulfilled by the data and it is evident that equations 2, 3, and 4 can not apply to this case.

Column 8 gives the concentration of silica calculated to be in excess of that required to form the compound $Ca(H_3SiO_4)_2$ with the total lime present. Data in columns 2, 5, and 8 permit calculation of the hydrolysis constant,

$$K_{h_4}=\frac{[H_4SiO_4][OH^-]}{[H_3SiO_4^-]} \qquad (1a)$$

for the equation:

$$Ca(H_3SiO_4)_2 + 2H_2O \rightleftharpoons 2H_4SiO_4 + Ca(OH)_2 \quad (1)$$

Thus, for each mol of uncombined lime given in column 5, the solution must contain 2 mols of hydroxyl ion and 2 mols of H_4SiO_4 as expressed by the equation. The total silicic acid includes also the quantity calculated to be present in solution in excess of $Ca(H_3SiO_4)_2$. For each mol of combined lime, represented by the difference of the quantities in columns 2 and 5, the solution must contain 2 mols of $H_3SiO_4^-$. The concentrations $[H_4SiO_4]$, $[OH^-]$, $[H_3SiO_4^-]$, may thus be readily obtained from the data and values of K_{h_4} calculated.

For example, the calculation of K_{h_4} for solution 1 of table 3 was performed as follows: $[OH^-] = \frac{0.00267}{\frac{1}{2}\,CaO}$; $[H_4SiO_4] = \frac{0.1324}{SiO_2} + \frac{0.00267}{\frac{1}{2}\,CaO}$; $[H_3SiO_4^-] = 2\left(\frac{0.0846 - 0.00267}{CaO}\right)$, where SiO_2 and CaO represent the molecular weights of silica and lime, respectively.

Then $K_{h_4} = \dfrac{\left(\frac{0.00267}{\frac{1}{2}\,CaO}\right)\left(\frac{0.1324}{SiO_2} + \frac{0.00267}{\frac{1}{2}\,CaO}\right)}{2\left(\frac{0.0846 - 0.00267}{CaO}\right)} = 7.44 \times 10^{-5}$, as given in column 9.

The absence of a general trend of increase or decrease in K_{h_4} as the solutions undergo an approximately 15-fold variation in concentration, and the constancy of these values within the experimental accuracy, justify the conclusion that equation 1 represents the equilibrium involved, i.e., the hydrolysis of a calcium silicate having the molar ratio $CaO/SiO_2 = 0.5$, to calcium hydroxide and silicic acid.

4. HYDROLYSIS OF CaH_2SiO_4

In order that the hydrolysis of CaH_2SiO_4 may proceed only to $Ca(H_3SiO_4)_2$ a sufficiently high concentration of calcium hydroxide must be present to repress the further hydrolysis to H_4SiO_4. To investigate the region where this condition occurs emf measurements were obtained for solutions whose compositions lie on the line OP of figure 3 as well as at lime concentrations intermediate between MN and OP, these compositions being prepared by adding calcium hydroxide to members of the MN series. The molar ratios of combined lime to total silica in the solutions was found to be approximately 0.5, indicating that they contained predominately $Ca(H_3SiO_4)_2$ with CaH_2SiO_4 and H_4SiO_4 probably also being present in smaller concentrations. Hence no satisfactory value of the hydrolysis constant of the equilibrium between CaH_2SiO_4 and $Ca(H_3SiO_4)_2$ could be obtained in this region.

Therefore, a series of compositions (table 4) lying on the line QR of figure 3 was prepared at a somewhat higher lime concentration (0.1750 g CaO per l). Although these solutions were highly supersaturated with respect to hydrated calcium silicate all but the first three or four of table 4 remained stable for many hours with no trace of precipitation.

TABLE 4.—*Data used in determining the hydrolysis constant K_{h3} of the reaction*

$$2CaH_2SiO_4+2H_2O \rightleftarrows Ca(H_3SiO_4)_2+Ca(OH)_2$$

[Lime concentration=0.1750 g CaO per l in all solutions]

1	2	3	4	5	6	7	8
No.	Concentration of SiO_2	emf of cell	CaO corresponding to emf	pH	Molar ratio of combined CaO to total SiO_2 in solution	CaO in excess of CaH_2SiO_4	$K_{h3}\times10^3$
	g/l	*v*	*g/l*			*g/l*	
1	0.2876	0.89582	0.0337	10.85	0.53	None	
2	.2634	.90024	.0406	10.92	.55	None	
3	.2418	.90598	.0497	11.02	.56	None	
4	.2205	.90947	.0557	11.08	.58	None	
5	.1985	.9112	.0608	11.10	.62	None	
6	.1776	.9150	.0708	11.17	.63	0.0091	7.3
7	.1571	.9182	.0804	11.22	.64	.0282	7.1
8	.1367	.9210	.0910	11.27	.66	.0473	7.1
9	.1166	.9231	.1006	11.30	.68	.0661	6.2
10	.0966	.9249	.1093	11.33	.73	.0848	4.6
11	.0788	.9275	.1218	11.38	.71	.1013	5.5
12	.0574	.9296	.1344	11.41	.76	.1110	4.5
Average							6.0×10^{-3}

If calcium hydroxide is present in sufficient concentration in these solutions to prevent the hydrolysis of CaH_2SiO_4 to H_4SiO_4 the potential measurements recorded in table 4 are given by the cell,

$$H_2 \left| \begin{matrix} Ca(OH)_2 \\ CaH_2SiO_4 \\ Ca(H_3SiO_4)_2 \end{matrix} \right| KCl\ (saturated) \left| HgCl+Hg, \right.$$

from which the hydrolysis constant,

$$K_{h3}=\frac{[H_3SiO_4^-]\,[OH^-]}{[H_2SiO_4^-]}, \tag{2a}$$

of the reaction:

$$2CaH_2SiO_4+2H_2O \rightleftarrows Ca\ (H_3SiO_4)_2+Ca(OH)_2, \tag{2}$$

may be calculated.

Column 6 of table 4 gives the molar ratios of combined lime to total silica and these values lie between 1, corresponding to the compound CaH_2SiO_4, and 0.5, corresponding to the compound $Ca\ (H_3SiO_4)_2$. It is evident that equation 2 only can apply to this equilibrium. Column 7 contains the lime in excess of that required by the silica to form the compound CaH_2SiO_4. No calculation of K_{h3} was attempted for those solutions which contained less total lime than corresponds to this compound. The method of calculating values of K_{h3} given in column 8 will be made clear by the following example:

$$\text{Solution no. 6:}[OH^-]=\frac{0.0708}{1/2\ CaO};\ [H_3SiO_4^-]=\frac{0.0708-0.0091}{1/2\ CaO};$$

$$[H_2SiO_4^-]=\frac{0.1776}{SiO_2}-[H_3SiO_4^-];\ K_{h3}=7.3\times10^{-3}.$$

The satisfactory agreement of the values of K_{h3} thus calculated justifies the application of equation 2 to this equilibrium.

5. HYDROLYSIS OF $Ca_3(HSiO_4)_2$

Figure 2 indicates that with a concentration of lime relatively high compared to the concentration of silica the molar ratio of combined lime to silica may exceed unity. If such combinations represent the neutralization of a definite silicic acid by calcium hydroxide then it is necessary to assume that the acid has more than two replaceable hydrogens.

To investigate solutions of higher proportion of combined lime to silica the series represented by the line ST in figure 3 was prepared. These solutions were highly supersaturated and unstable and, in the case of the first two, the equilibrium reading of potential was not obtained until after precipitation of hydrated calcium silicate had begun. The molar ratios of combined lime to silica of approximately unity given by these measurements indicated that CaH_2SiO_4 is present in these solutions probably together with lower concentrations of $Ca(H_3SiO_4)_2$ and $Ca_3(HSiO_4)_2$.

It had been noticed repeatedly that precipitation from unstable silicate solutions during measurement on the cell,

$$H_2 \left| \begin{matrix} Ca(OH)_2 \\ Ca\ silicate \end{matrix} \right| KCl\ (saturated) \left| HgCl + Hg, \right.$$

produced no apparent change in the emf when the concentration of lime was such that the amount of silica remaining in solution after precipitation was very small. This fact indicates that the amount of free calcium hydroxide in solution is unchanged by precipitation of calcium silicate and that the molar ratio of combined lime to silica in solution after precipitation is the same as that in the initial solution. As the calcium silicate solutions at the higher lime concentrations are very unstable it was necessary to make the assumption that the emf reading obtained, even after precipitation, represented conditions in the initial clear solution.

Table 5 gives data for solutions prepared at a concentration of 0.5 g CaO per l (UV, fig. 3). The molar ratio of combined CaO to SiO_2 (column 6) indicates that the values for emf (column 3) were produced by the cell,

TABLE 5.—*Data used in determining the hydrolysis constant* Kh_2 *of the reaction:* $Ca_3(HSiO_4)_2 + 2H_2O \rightleftarrows 2CaH_2SiO_4 + Ca(OH)_2$

[Lime concentration=0.5000 g CaO per l in all solutions]

1	2	3	4	5	6	7	8
No.	Concentration of SiO_2	emf of cell	CaO corresponding to emf	pH	Molar ratio of combined CaO to total SiO_2 in solution	CaO in excess of $Ca_3(HSiO_4)_2$	$Kh_2 \times 10^2$
	g/l	*v*	*g/l*			*g/l*	
1	0.1915	0.94867	0.2950	11.73	1.12	0.2418	1.5
2	.1754	.94934	.3019	11.74	1.21	.2543	1.5
3	.1610	.95064	.3228	11.76	1.18	.2745	2.1
4	.1468	.95148	.3349	11.78	1.20	.2944	1.7
5	.1328	.95273	.3527	11.80	1.19	.3140	2.1
6	.1189	.95372	.3671	11.81	1.20	.3335	2.0
7	.1051	.95440	.3773	11.82	1.22	.3528	1.3
8	.0915	.95502	.3877	11.83	1.31	.3718	0.8
9	.0780	.95620	.4063	11.85	1.29	.3907	1.1
10	.0646	.95724	.4247	11.87	1.25	.4095	1.5
11	.0514	.95814	.4391	11.89	1.27	.4280	1.4
Average							1.5×10^{-2}

$$H_2 \left| \begin{matrix} Ca(OH)_2 \\ Ca_3(HSiO_4)_2 \\ CaH_2SiO_4 \end{matrix} \right| KCl \text{ (saturated)} \quad HgCl + Hg,$$

sufficient calcium hydroxide being present to repress further hydrolysis of CaH_2SiO_4.

The calculation of K_{h_2} for the mass action expression,

$$K_{h_2} = \frac{[H_2SiO_4^{=}]\,[OH^-]}{[HSiO_4^{\equiv}]}, \tag{3a}$$

of the equilibrium,

$$Ca_3(HSiO_4)_2 + 2H_2O \rightleftarrows 2CaH_2SiO_4 + Ca(OH)_2, \tag{3}$$

was performed by the same method as that used in calculating K_{h_3}. Considering the experimental difficulties involved in obtaining data on calcium silicate solutions at the higher lime concentrations the values of K_{h_2} (column 8) thus obtained are in satisfactory agreement. They support the assumption that the equilibrium is one between two salts of orthosilicic acid having the molar ratios CaO/SiO_2 of 3:2 and 1:1, respectively.

6. HYDROLYSIS OF Ca_2SiO_4

A series of four solutions was prepared to investigate the hydrolysis of Ca_2SiO_4 to the next lower calcium silicate, $Ca_3(HSiO_4)_2$. Table 6 summarizes the data. Column 7 shows that the molar ratio of combined lime to silica is intermediate between 2:1 and 3:2 in agreement with the equation,

$$2Ca_2SiO_4 + 2H_2O \rightleftarrows Ca_3(HSiO_4)_2 + Ca(OH)_2 \tag{4}$$

Evidently the electromotive forces recorded in column 4 represent measurements upon the cell,

$$H_2 \left| \begin{matrix} Ca(OH)_2 \\ Ca_2SiO_4 \\ Ca_3(HSiO_4)_2 \end{matrix} \right| KCl \text{ (saturated)} \mid HgCl + Hg.$$

Values of K_{h_1} are recorded in column 9 and the agreement for the four solutions indicates that equation 4 represents the equilibrium involved.

Theoretically K_{h_1} should have a higher value than K_{h_2} but it is seen that the value obtained is somewhat lower. The accuracy of the method is, however, not sufficiently great to differentiate between these two constants and it can only be said that they are of the same order of magnitude.

7. THE IONIZATION CONSTANTS OF ORTHOSILICIC ACID

Orthosilicic acid is assumed to ionize in four stages represented by the following equations;

TABLE 6.—*Data used in determining the hydrolysis constant* K_{h1} *of the reaction:* $2Ca_2SiO_4 + 2H_2O \rightleftarrows Ca_3(HSiO_4)_2 + Ca(OH)_2$

1	2	3	4	5	6	7	8	9
No.	Composition of solutions		emf of cell	CaO corresponding to emf	pH	Molar ratio of combined CaO to total SiO_2 in solution	CaO in excess of Ca_2SiO_4	$K_{h_1} \times 10^2$
	CaO	SiO_2						
	g/l	*g/l*	*v*	*g/l*			*g/l*	
1	0.8500	0.0886	0.96864	0.6988	12.06	1.83	0.6846	1.3
2	.8750	.0812	.96986	.7353	12.08	1.84	.7233	1.2
3	.9000	.0739	.97107	.7717	12.10	1.86	.7620	1.1
4	.9250	.0665	.97226	.8100	12.12	1.85	.8008	1.2
Average								1.2×10^{-2}

$$H_4SiO_4 \rightleftarrows H^+ + H_3SiO_4^- \quad (5)$$

$$H_3SiO_4^- \rightleftarrows H^+ + H_2SiO_4^= \quad (6)$$

$$H_2SiO_4^= \rightleftarrows H^+ + HSiO_4^{\equiv} \quad (7)$$

$$HSiO_4^{\equiv} \rightleftarrows H^+ + SiO_4^{\equiv} \quad (8)$$

To equation 5 corresponds the mass action expression,

$$K_{a_1} = \frac{[H^+]\,[H_3SiO_4^-]}{[H_4SiO_4]}.$$

But from the equation la, $[H_3SiO_4^-] = \dfrac{[H_4SiO_4]\,[OH^-]}{K_{h_4}}$

and substitution of this quantity gives:

$$K_{a_1} = \frac{[H^+]\,[OH^-]}{K_{h_4}} = \frac{K_w}{K_{h_4}} \quad (5a)$$

Similarly:

$$K_{a_2} = \frac{[H^+]\,[H_2SiO_4^=]}{[H_3SiO_4^-]} = \frac{K_w}{K_{h_3}} \quad (6a)$$

$$K_{a_3} = \frac{[H^+]\,[HSiO_4^{\equiv}]}{H_2SiO_4^=} = \frac{K_w}{K_{h_2}} \quad (7a)$$

$$K_{a_4} = \frac{[H^+]\,[SiO_4^{\equiv}]}{[HSiO_4^{\equiv}]} = \frac{K_w}{K_{h_1}} \quad (8a)$$

Thus the four ionization constants of orthosilicic acid may be calculated from the hydrolysis constants of its salts and the ionization constant of water.

Using the value, $K_w = 1.47 \times 10^{-14}$, for the ionization constant of water at 30 C [21] and the average values of the hydrolysis constants of

[21] H. S. Harned, The Ionization Constant of Water and the Dissociation of Water in Potassium Chloride Solutions from Electromotive Forces of Cells Without Liquid Junction, Jour. Am. Chem. Soc., vol. 55, pp. 2194-2206, 1933.

the four calcium salts of orthosilicic acid: $K_{h_4}=6.8\times10^{-5}$, $K_{h_3}=6.0\times10^{-3}$, $K_{h_2}=1.5\times10^{-2}$, and $K_{h_1}=1.2\times10^{-2}$, the following values of the constants for the first, second, third, and fourth stages in the ionization of orthosilicic acid were obtained: $K_{a_1}=2.2\times10^{-10}$, $K_{a_2}=2.0\times10^{-12}$, $K_{a_3}=1\times10^{-12}$, and $K_{a_4}=1\times10^{-12}$.

Harman [22] measured the hydrolysis of sodium metasilicate in aqueous solution by electrometric determinations of hydroxyl ion concentration and obtained 1.6×10^{-10} and 5.1×10^{-17} for the primary and secondary ionization constants of silicic acid. By electrometric titration of sodium silicate solution with hydrochloric acid he obtained $K_{a_1}=2.2\times10^{-10}$. Electrometric methods for determing the degree of hydrolysis of sodium silicates were applied by Bogue [23] who derived for K_{a_1} the values 4.8 to 18.3×10^{-10} and for K_{a_2}, 5.2 to 16.7×10^{-12}. Hägg [24] by a similar procedure estimated that $K_{a_1}=10^{-9}$, $K_{a_2}=10^{-13}$.

Britton [25] prepared titration curves by neutralizing sodium silicate solutions with hydrochloric acid and concluded from their form that the mode of ionization of silicic acid cannot be expressed in terms of ionization constants. However, Joseph and Oakley [26] prepared a similar curve and asserted it to be typical of the combination of a strong base with a weak dibasic acid. From inflections of their curve they derived the values $K_{a1}=10^{-10}$ and $K_{a2}=10^{-12}$. Treadwell and Wieland [27] also constructed titration curves and obtained $K_{a1}=10^{-9.7}$, $K_{a2}=10^{-12}$.

Despite the absence of good agreement, the results of these investigators indicate that the primary and secondary ionization constants of silicic acid are of the magnitude, $K_{a1}=10^{-10}$ and $K_{a2}=10^{-12}$, thus checking roughly the values obtained in this study.

In figure 4 are titration curves prepared from electrometric measurements upon solutions having compositions on the lines MN, OP, QR, ST, and UV in figure 3. The curves of figure 4 show the change in emf as solutions of initial compositions lying on the line MN (fig. 3) are titrated with calcium hydroxide solution. The curve for calcium hydroxide solutions constructed from data in table 2 is also plotted in figure 4. A comparison of the emf of the cell containing calcium hydroxide at any definite concentration to that of the cell containing also calcium silicate in solution at the same total lime concentration illustrates graphically the marked effect of the dissolved silica in lowering the emf and pH.

8. DISCUSSION OF RESULTS WITH REFERENCE TO SOLUBILITY RELATIONSHIPS IN THE SYSTEM CaO–SiO_2–H_2O

It has been shown in the preceding sections that the constitution of solutions in the region of the curve CDE (fig. 1) is governed by the equilibrium, $Ca(H_3SiO_4)_2+2H_2O\rightleftharpoons 2H_4SiO_4+2Ca(OH)_2$. The value

[22] R. W. Harman, Aqueous Solutions of Sodium Silicates, VII, Jour. Phys. Chem., vol. 31, pp. 616–625, 1925.
[23] R. H. Bogue, The Hydrolysis of the Silicates of Sodium, Jour. Am. Chem. Soc., vol. 42, pp. 2575–2582, 1920.
[24] G. Hägg, The Hydrolysis of the Sodium Silicates, Zs. anorg. allgem. Chem., vol. 155, pp. 21–41, 1926.
[25] H. T. S. Britton, Electrometric Study of the Precipitation of Silicates, Jour. Chem. Soc., pp.425–436, 1927.
[26] A. F. Joseph and H. B. Oakley, The Action of Silica on Electrolytes, Jour. Chem. Soc., vol. 127, pp. 2813–2818, 1925
[27] W. D. Treadwell and W Wieland, The Hydrates of Silicic Acid, Helv. Chim. Acta, vol. 13, pp. 842–864, 1930.

of the hydrolysis constant of this reaction was determined by setting up the proper relationship between total silica, total lime, and uncombined calcium hydroxide in the solutions studied. Using the value of this constant and the concentrations of total lime and silica in any solution for which the above equilibrium is valid, the hydroxyl ion concentration may be computed from the following easily derived equation:

$$[OH^-]=-1/2([SiO_2]-2[CaO]+K_{h4})+1/2\sqrt{([SiO_2]-2[CaO]+K_{h4})^2+8[CaO]K_{h4}}$$

in which $[SiO_2]$ and $[CaO]$ are molar concentrations of silica and lime, respectively, and $K_{h4}=6.8\times10^{-5}$. The amount of lime combined as calcium disilicate may then be computed as well as the concentrations of silicate ion and silicic acid. Such calculations are presented in table 7 for compositions on the curve CDE and it is shown there that the concentration of $H_3SiO_4^-$ reaches a maximum value between D and

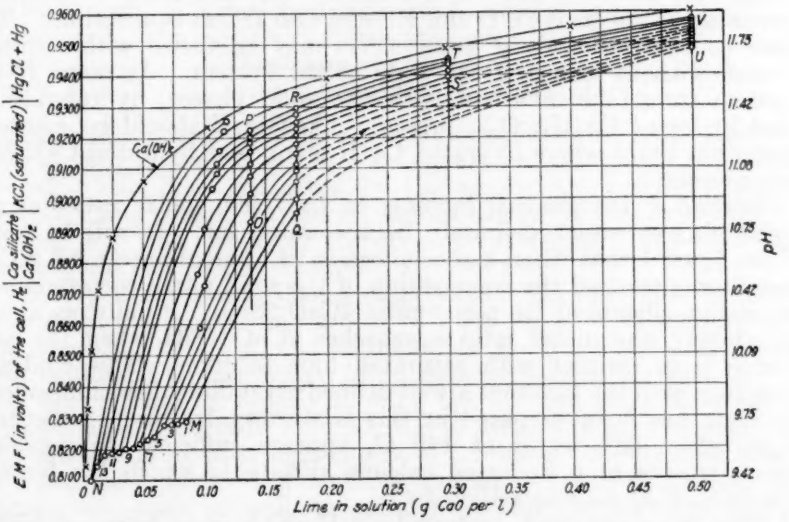

FIGURE 4.—*Electrometric titration curves showing the effect of adding calcium hydroxide to lime-silica solutions.*

E (fig. 1) while that of H_4SiO_4 has its maximum value to the left of D and thereafter decreases sharply. No calculations are presented for the concentrations of the various constituents at E or along the curve EF where an overlapping of two steps in the hydrolysis undoubtedly occurs.

TABLE 7.—*Molar concentrations of* OH^-, $H_3SiO_4^-$, *and* H_4SiO_4 *in solutions on curve CDE, figure 1, which are governed by the equilibrium:* $Ca(H_3SiO_4)_2+2H_2O\rightleftharpoons 2H_4SiO_4+Ca(OH)_2$

No.	$[OH^-]$ $\times10^5$	$[H_3SiO_4^-]$ $\times10^3$	$[H_4SiO_4]$ $\times10^3$	No.	$[OH^-]$ $\times10^5$	$[H_3SiO_4^-]$ $\times10^3$	$[H_4SiO_4]$ $\times10^3$
1	3.2	0.94	2.01 (C)	5	5.6	2.49	2.98 (D)
2	3.6	1.05	2.01	6	9.2	2.95	2.16
3	3.5	1.32	2.58	7	19.2	3.21	1.14
4	3.3	1.50	3.14	8	32.4	3.04	0.64 (E)

It does not necessarily follow, of course, that the composition of the solid phases, whose solubility is represented by the curve CDE, is governed by the equilibrium, $Ca(OH)_2+2H_4SiO_4 \leftrightarrows Ca(H_3SiO_4)_2+2H_2O$, yet the available evidence indicates that such is the case, for it has already been pointed out (p. 756) on the basis of the molar ratios in the solid phases that the curve CD appears to represent the compositions of solutions saturated with respect to hydrated silica and DE with respect to a calcium disilicate, $CaO \cdot 2SiO_2$. Along EF where the equilibrium, $Ca(OH)_2+Ca(H_3SiO_4)_2 \leftrightarrows 2CaH_2SiO_4+2H_2O$, is involved, the molar ratios indicate that the solid phase is a monocalcium silicate, $CaO \cdot SiO_2$. To indicate their possible derivation from orthosilicic acid these compounds may be assigned the formulas, $Ca(H_3SiO_4)_2$, and CaH_2SiO_4, respectively, each possessing an unknown degree of hydration.

In a ternary system at constant temperature and pressure one solid phase in contact with solution makes the system univariant. This condition, although not experimentally realized along DE, should occur along the curves CD and EF and also DE at equilibrium. The lime concentration along these curves may be varied within certain limits, without changing the state of the system. At point D the system should be invariant with two solid phases, hydrated silica and hydrated $Ca(H_3SiO_4)_2$, present; likewise E should be a second invariant point where hydrated $Ca(H_3SiO_4)_2$ and hydrated CaH_2SiO_4 are present.

Beyond F the gradual increase in CaO/SiO_2 molar ratios of the solid phases cannot definitely be accounted for. It will be noted from figure 1 that when a concentration of approximately 0.7 g CaO per liter is reached the composition of the solid phase corresponds to a calcium silicate of the molar ratio $3CaO:2SiO_2$. Finally, as shown previously, the molar ratio approaches $2CaO:1SiO_2$ when the solid phase is in contact with saturated lime solution. This evidence, together with the fact that a well-defined crystalline dicalcium silicate hydrate has been prepared in this laboratory by reaction between lime, silica, and water at 150 C, appears sufficient to postulate the existence of a hydrated calcium silicate to which the formula $Ca_2SiO_4 \cdot nH_2O$ may be assigned.

That the compound, hydrated $Ca(H_3SiO_4)_2$, may have solubilities lying on or to the right of an extension of DE was indicated by the great stability of solutions prepared in this region, which showed no precipitation even after several months. Such solutions would be supersaturated with reference to the solubility curve EF but would be stable in the absence of appreciable quantity of solid hydrated CaH_2SiO_4. An attempt was made to work out such a curve by analyzing solutions resulting after spontaneous precipitation from mixtures on the lines OP and QR, figure 3. The resultant compositions fell to the right of an extension of DE but could not well be represented by a curve. Apparently equilibrium is not readily attained by precipitation from the slightly supersaturated solutions.

IV. REACTION OF WATER ON THE ANHYDROUS CALCIUM SILICATES

1. METHOD OF PROCEDURE

Binary compounds of lime and silica are the chief constituents of portland cement and their reaction with water plays an important part in setting. The study described herein will deal with the mechanism of this reaction and with the relationship of the products to equilibrium conditions in the system $CaO–SiO_2–H_2O$. It will also attempt to show that the hydraulic properties of the anhydrous calcium silicates are intimately related to their capacity to form solutions supersaturated with respect to the hydrated calcium silicates.

The following anhydrous compounds were prepared from chemically pure calcium carbonate and silica by methods already described:[28]

Monocalcium silicate — $CaO·SiO_2$
Tricalcium disilicate — $3CaO·2SiO_2$
γ–Dicalcium silicate — γ–$CaO·SiO_2$
β–Dicalcium silicate — β–$2CaO·SiO_2$
Tricalcium silicate — $3CaO·SiO_2$

Chemical analyses and petrographic examination of the products showed their lime-silica ratios to be correct and the purity to be that desired. Free lime, measured by the ammonium acetate titration method,[29] was present in the tricalcium silicate to the extent of 0.3 percent, but was absent in the other preparations. The materials were ground and passed through a no. 200 sieve.

The experiments described in this section are analogous to those reported in a study of the reaction of water on calcium aluminates.[30] The procedure followed was to shake the finely ground compounds with distilled CO_2-free water for a definite period of time and to stop the reaction by rapidly filtering the solution from the residue. A proportion of 20 grams solid per liter of water was used throughout. Immediately after filtering samples of the clear filtrates were taken for chemical analysis of their lime and silica contents and the remainder set aside in well-stoppered flasks for further observation. In most cases the extent of combination between lime and silica in solution was also determined by the electrometric method already described.

2. REACTION OF WATER ON MONOCALCIUM SILICATE ($CaO·SiO_2$)

The compositions of solutions derived from monocalcium silicate are shown in figure 5 for increasing periods of contact of the solid with the solution.

The guide lines marked $1CaO:1SiO_2$, $2CaO:1SiO_2$, and $3CaO:1SiO_2$ in this figure indicate the compositions of solutions which would contain lime and silica in these ratios. The displacement of the curve for solutions derived from monocalcium silicate to the right of the $1CaO:1SiO_2$ guide line shows that the solutions contain an amount of

[28] B. S. Technologic Papers Nos. 43 and 78.
[29] W. Lerch and R. H. Bogue, Revised Procedure for the Determination of Uncombined Lime in Portland Cement, Ind. & Eng. Chem., anal. ed., vol. 2, p. 296, 1930.
[30] See footnote 6, p. 754.

lime slightly greater than that corresponding to the molar ratio of the anhydrous compound.

The monocalcium silicate forms apparently stable solutions which may stand for months without appreciable change in composition, differing in this respect, as will be shown later, from the more basic anhydrous calcium silicates, all of which form metastable solutions capable of spontaneous precipitation. As the more basic compounds are hydraulic while monocalcium silicate is nonhydraulic,[31] it appears that the property of metastable solubility is closely connected with the capacity of calcium silicates to set and harden.

However, figure 9, which indicates the relationship of solutions derived from the calcium silicates to equilibrium conditions in the system CaO–SiO_2–H_2O, shows that solutions derived from anhydrous

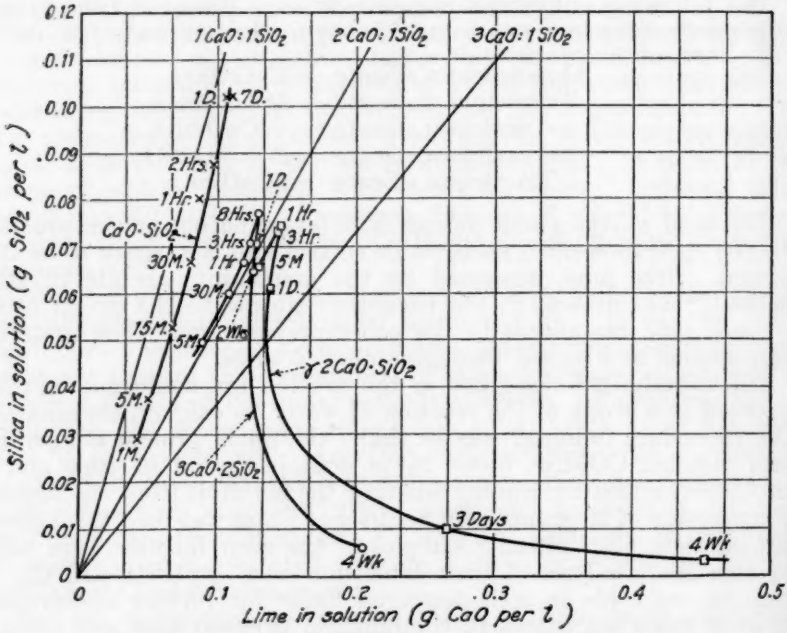

FIGURE 5.—*Showing the compositions of solutions derived from* $CaO{\cdot}SiO_2$, $3CaO{\cdot}2SiO_2$, *and* γ–$2CaO{\cdot}SiO_2$ *after increasing time of contact with water.*

monocalcium silicate lie in a region of supersaturation with respect to hydrated monocalcium silicate. But in the absence of this phase such solutions are relatively stable. When hydration of the anhydrous compound starts, or if solutions are placed in contact with solid hydrated monocalcium silicate, precipitation should occur until points on the lower solubility curve EF are reached.

It was actually found that solutions which had remained in contact with solid anhydrous $CaO \cdot SiO_2$ for periods of a month or more had compositions closer to the curve EF, indicating possibly that hydration of the anhydrous compound had begun. This behavior differs from that of the more basic lime silicates which contribute lime greatly in excess of the ratio $1CaO : 1SiO_2$ to solution by continued

[31] A. A. Klein and A. J. Phillips, The Hydration of Portland Cement, B.S. Technologic Paper No. 43.

hydrolysis, eventually, in the case of the 3:1 and 2:1 calcium silicates, producing a solution saturated with calcium hydroxide if a sufficient quantity of the silicate were present originally.

Electrometric measurements, which showed that the molar ratio of combined lime to silica in this region was approximately 0.5, indicated that $Ca(H_3SiO_4)_2$ is the principal product of the hydrolysis of monocalcium silicate. Thus it appears that anhydrous monocalcium silicate cannot be said to have a true solubility but rather one that is incongruent.

3. REACTION OF WATER ON TRICALCIUM DISILICATE ($3CaO \cdot 2SiO_2$)

Tricalcium disilicate is only obtained by crystallization from a melt of the proper composition[32] and hence cannot be a constituent of portland cement. Its reaction with water, however, illustrates the development of the property of metastable solubility with increase in the basicity of the calcium silicates.

Figures 5 and 9 show that the amount of dissolved silica derived from tricalcium disilicate first increases to a maximum with time of contact of the anhydrous solid with the solution, then drops off sharply with a subsequent gradual increase in the concentration of lime. Initially the reaction appears to involve mainly the formation of supersaturated solutions, followed by precipitation at a rate exceeding that of solution. Thereafter the lime concentration in solution increases through the momentary solution of the anhydrous compound followed by precipitation of hydrated calcium silicate of lower lime-silica molar ratio. The final solid product of this reaction would be hydrated tricalcium disilicate. Electrometric measurements of the compositions shown in figure 5 derived from tricalcium disilicate showed that at these concentrations lime is combined with silica in molar ratios of 0.8 – 0.9, indicating that these solutions contain mixtures of CaH_2SiO_4 and $Ca(H_3SiO_4)_2$.

It appears then that tricalcium disilicate differs from monocalcium silicate in its ability to form supersaturated solutions capable of spontaneous decomposition. This property, according to Le Chatelier,[33] is characteristic of hydraulic materials and thus these experiments indicate that the 3:2 calcium silicate should be feebly hydraulic.

4. REACTION OF WATER ON GAMMA-DICALCIUM SILICATE (γ–$2CaO \cdot SiO_2$)

Dicalcium silicate occurs in cement predominantly in the unstable beta form.[34] The gamma modification is the stable form at ordinary temperatures and is known to be comparatively unreactive. Thus Newberry and Smith [35] found that γ–$2CaO \cdot SiO_2$ was not appreciably hydrolyzed after long contact with water and only slightly hydrated. Klein and Phillips [36] likewise concluded that the compound is non-hydraulic. Lerch and Bogue,[37] however, showed that its reaction

[32] G. A. Rankin and F. E. Wright, The Ternary System $CaO-Al_2O_3-SiO_2$, Am. Jour. Sci. Series 4, vol. 39, p. 6, 1915.
[33] See footnote 3, p. 752.
[34] See footnote 2, p. 752.
[35] S. B. Newberry and M. M. Smith, Studies on the Constitution of Hydraulic Cements, Cement & Eng News, vol. 13, p. 66, 1902.
[36] See footnote 31, p. 772.
[37] W. Lerch and R. H. Bogue, Studies on the Hydrolysis of Compounds Which May Occur in Portland Cement, Jour. Phys. Chem., vol. 31, pp. 1627–1646, 1927.

with water, though slow, does not differ in type from that of β–$2CaO \cdot SiO_2$ and $3CaO \cdot SiO_2$ and that it hydrolyzes even in saturated lime solution.

Figure 5 shows that the reaction of γ–$2CaO \cdot SiO_2$ with water is very similar to that of $3CaO \cdot 2SiO_2$ but somewhat more rapid. Both form metastable solutions capable of spontaneous precipitation. The relationship of the compositions of solutions derived from this compound to equilibrium conditions is indicated in figure 9. Initially the γ–$2CaO \cdot SiO_2$ is hydrolyzed, giving solutions containing principally CaH_2SiO_4 as indicated by electrometric measurements. As γ–$2CaO \cdot SiO_2$ can hydrolyze even in saturated lime solution, it is to be expected that the final product in equilibrium with the solution would be hydrated Ca_2SiO_4 and hydrated $Ca_3(HSiO_4)_2$ when the amount of lime in the silicate initially present is large compared with that required to saturate the solution.

It thus appears that there has been an increase in hydraulic characteristics in passing from tricalcium disilicate to γ–dicalcium silicate.

5. REACTION OF WATER ON BETA-DICALCIUM SILICATE (β–$2CaO \cdot SiO_2$)

Experiments of Klein and Phillips [38] led them to believe that β–dicalcium silicate hydrates very slowly without the liberation of lime by hydrolysis. However, the conclusion is at variance with the results of other investigators [39] who found that this compound undergoes both hydrolysis and hydration, when placed in contact with water. According to Bates and Klein [40] β–$2CaO \cdot SiO_2$ sets slowly but after 28 days attains sufficient strength to be almost upon an equality with tricalcium silicate.

The reaction of this compound with water is illustrated in figure 6. The rate of reaction is much greater than that of γ–$2CaO \cdot SiO_2$ and the solutions formed were more highly supersaturated with respect to the hydrated products, as the comparison of their compositions with equilibrium conditions afforded by figure 9 indicates. Precipitation from the solutions containing the highest concentrations of silica started within a half hour. The course of precipitation from the unstable to the corresponding equilibrium states and the molar ratios of lime to silica in the precipitates are indicated in figure 6. The precipitates were similar in appearance to those formed by precipitation from mixtures having compositions represented by points on the line AB in figure 9.

The molar ratios of combined lime to silica in solution given by electrometric measurements showed that the dicalcium silicate gives solutions containing CaH_2SiO_4 with increasing amounts of $Ca_3(HSiO_4)_2$ being formed as the lime concentration increases. The final insoluble product of the reaction when a saturated lime solution had been formed should have a composition approaching the molar ratio $2CaO:1SiO_2$ of hydrated calcium orthosilicate, when the quantity of anhydrous silicate originally present is sufficiently large. On the other hand, with insufficient anhydrous calcium silicate initially present to form a saturated lime solution, the molar ratio of lime to

[38] See footnote 31, p. 772.

[39] Lerch and Bogue, see footnote 34; T. Thorvaldson and V. Vigfusson, Action of Water on Tricalcium Silicate and Beta-Dicalcium Silicate, Trans. Roy. Soc. Can. series 3, vol. 22, pp. 423–431, 1928.

[40] P. H. Bates and A. A. Klein, Properties of the Calcium Silicates and Calcium Aluminate Occurring in Normal Portland Cement, B.S. Technologic Paper No. 78, 1917.

silica in the hydrated product would correspond to some other equilibrium relationship along the curve *BFEDC* of figure 9.

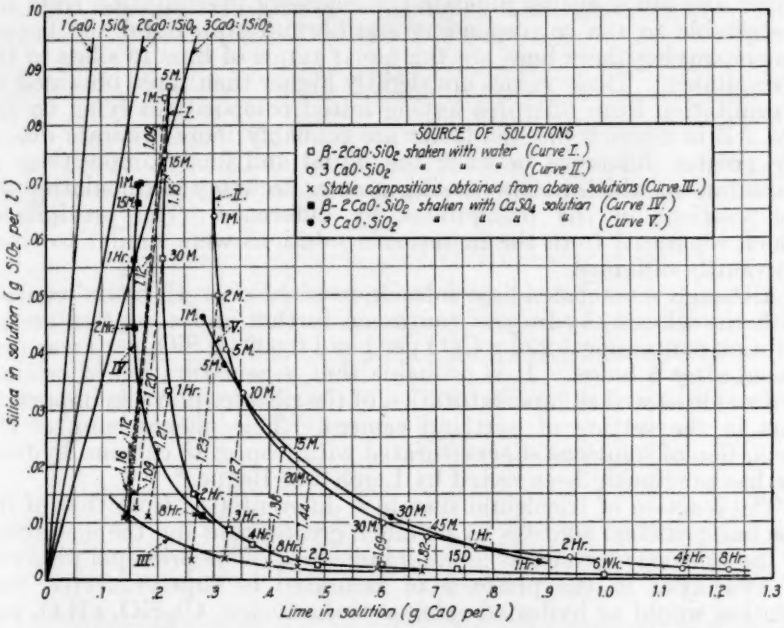
1CaO·1SiO2
2CaO·1SiO2
3CaO·1SiO2
SOURCE OF SOLUTIONS
□ β-2CaO·SiO2 shaken with water (Curve I.)
○ 3 CaO·SiO2 " " " (Curve II.)
× Stable compositions obtained from above solutions (Curve III.)
■ β-2CaO·SiO2 shaken with CaSO4 solution (Curve IV.)
● 3 CaO·SiO2 " " " " (Curve V.)
Silica in solution (g SiO2 per l)
Lime in solution (g CaO per l)

FIGURE 6.—*Showing the compositions of solutions derived from* β–$2CaO \cdot SiO_2$ *and* $3CaO \cdot SiO_2$ *after increasing time of contact with water and with calcium sulphate solution.*

6. REACTION OF WATER UPON TRICALCIUM SILICATE ($3CaO \cdot SiO_2$)

Le Chatelier [41] believed that the fundamental reaction in the hydration of portland cement is one between tricalcium silicate and water as follows: $3CaO \cdot SiO_2 + H_2O \rightarrow CaO \cdot SiO_2 \cdot 2\ 1/2H_2O + Ca(OH)_2$. Newberry and Smith [42] found that tricalcium silicate, in the presence of excess water, gives a residue of approximately the composition $3CaO \cdot 2SiO_2 \cdot 3H_2O$. Lerch and Bogue, and Thorvaldson and Vigfusson have studied the rate of reaction [43] between tricalcium silicate and water by determination of the lime liberated to solution at progressive time intervals. The two latter authors believed that hydrated 3:2 calcium silicate and hydrated monocalcium silicate were possible products of the reaction with water of both tricalcium silicate and β–dicalcium silicate.

Klein and Phillips [44] reported that tricalcium silicate hydrates readily with the formation of hydrated silicate and lime, and Bates and Klein [45] state that this compound has all the important properties of portland cement, especially those of "rate of setting" and strength developed.

[41] See footnote 3, p. 752.
[42] See footnote 35, p. 773.
[43] See footnote 39, p. 774.
[44] See footnote 31, p. 772.
[45] See footnote 40, p. 774.

The reaction of water with tricalcium silicate, illustrated in figure 6, is one of great rapidity, as might be expected in the case of such a highly basic compound. As before, lines connecting points on the upper and lower curves indicate the course of precipitation from the metastable to the corresponding equilibrium states and the figures accompanying these lines are the molar ratios of lime to silica in the precipitates. These values are slightly higher than those obtained by precipitation from mixtures having initial compositions lying on the line AB in figure 9 but the latter are probably more accurate due to the greater difference between the initial and final compositions of the solutions which makes possible greater accuracy in calculating the compositions of the precipitates by difference. The precipitates which separated from the metastable solutions were similar to those previously obtained.

Although a saturated lime solution resulted after 4½ hours' contact with the silicate, hydrolysis continued further and a supersaturated solution containing 1.226 g CaO per l and 0.0023 g SiO_2 per l was produced after 8 hours. It is probable that supersaturation of calcium hydroxide as well as supersaturation of the silicates plays an important part in the setting of portland cement. This phenomenon of the formation of solutions supersaturated with respect to calcium hydroxide has previously been noted by Lerch and Bogue.[46]

The reaction of tricalcium silicate is differentiated from that of the less basic calcium silicates by its much greater rate and the instability of the solutions formed as figure 9 indicates. The principal products of hydrolysis in the presence of saturated or supersaturated lime solution would be hydrated calcium orthosilicate, $Ca_2SiO_4 \cdot nH_2O$, and solid calcium hydroxide. Work in this laboratory has also shown that well-defined crystalline dicalcium silicate are formed by reaction between tricalcium silicate and water at 150 C and crystalline calcium hydroxide.

Figure 7 compares the rate of liberation of lime to solution by the different calcium silicates and illustrates clearly the rapidity of the reaction in the case of tricalcium silicate and the tendency of this compound to form supersaturated lime solutions. The curve for the hydrolysis of beta-di-calcium silicate is interesting in that the lime concentration in solution initially decreases with time of contact of the anhydrous solid. This is undoubtedly due to the precipitation of hydrated calcium silicate in this region removing more lime from solution than is being supplied by hydrolysis and solution of the anhydrous silicate.

The curves for the less basic silicates show the much slower rate of reaction of these compounds. It is seen that the reactivity of the calcium silicates increases in the following order: $CaO \cdot SiO_2$, $3CaO \cdot 2SiO_2$, γ–$2CaO \cdot SiO_2$, β–$2CaO \cdot SiO_2$, and $3CaO \cdot SiO_2$.

7. REACTION OF WATER ON PORTLAND CEMENT

The application of the foregoing methods to the reaction of water upon a commercial portland cement of the following composition was then investigated.

[46] See footnote 37, p. 773.

Oxide composition	Percent	Compound composition [47]	Percent
SiO_2	21. 58	$3CaO \cdot SiO_2$	67
Fe_2O_3	2. 81	$2CaO \cdot SiO_2$	11
Al_2O_3	4. 15	$3CaO \cdot Al_2O_3$	6
CaO	66. 22	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	8
MgO	2. 27	$CaSO_4$	3
SO_3	1. 93		
Ignition loss, 1.18%; insoluble, 0.08%; free lime, 0.4%.			

[47] R. H. Bogue, Calculation of Compounds in Portland Cement, Ind. & Eng. Chem., anal. ed., vol. 1, p. 192, 1929.

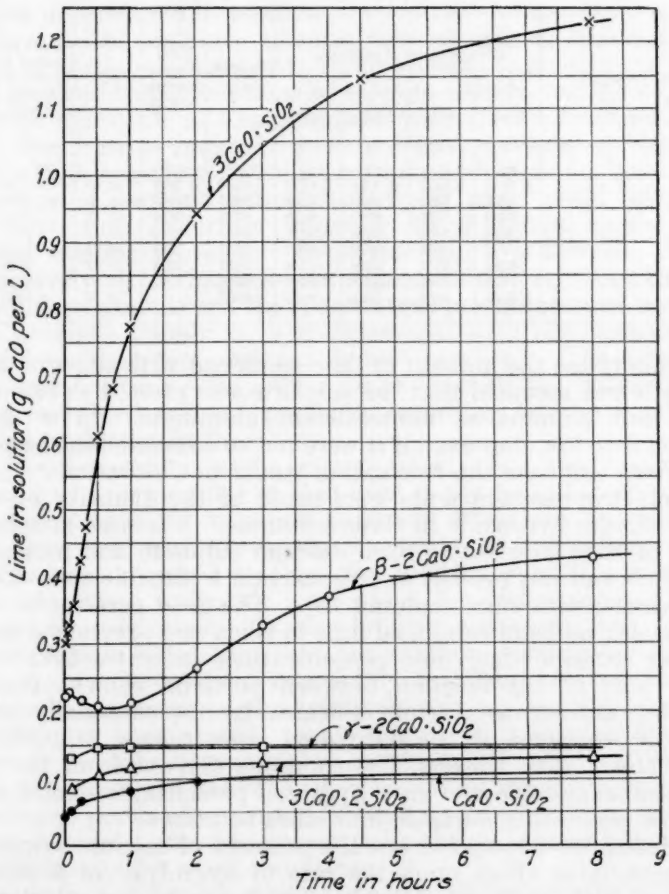

FIGURE 7.—*Showing the relative rates of liberation of lime to solution by the anhydrous calcium silicates.*

This cement was chosen because of its high tricalcium silicate content and freedom from alkalies.

Proceeding as in the study of the calcium silicates, shaking 20 grams of cement with a liter of water, gave the results contained in table 8. Columns 2, 3, 4, and 5 of this table give the compositions of the solutions for increasing time of contact between the cement and water

(column 1). Column 9 of this table shows that the lime concentration increased in 8 hours to give a solution highly supersaturated with respect to $Ca(OH)_2$. The sulphate of the cement was dissolved almost completely during the earlier periods but its concentration subsequently decreased. The alumina concentration was low at all time periods. Finally, the solutions contained concentrations of silica in metastable condition comparable to those supplied by tricalcium and β–dicalcium silicate at corresponding lime concentrations.

TABLE 8.—*Compositions and* pH *of solutions derived from a portland cement*

1	2	3	4	5	6	7	8	9	10
Time of contact	Composition of solutions				Emf of cell	CaO corresponding to emf	pH	CaO in excess of $CaSO_4$+ $CaO \cdot Al_2O_3$	Molar ratio of combined CaO/SiO_2 in solution
	CaO	SO_3	Al_2O_3	SiO_2					
	g/l	*g/l*	*g/l*	*g/l*	*v*	*g/l*		*g/l*	
1 min	0.5168	0.3423	0.0064	0.0234	0.9440	0.2464	11.65	0.2729	1.21
3 min	.5236	.3414	.0050	.0208	.9447	.2544	11.66	.2881	1.38
5 min	.5586	.3509	.0052	.0198	.9471	.2808	11.70	.3099	1.57
10 min	.5634	.3358	.0022	.0216	.9483	.2942	11.72	.3269	1.62
30 min	.5744	.3214	.0020	.0202	.9502	.3154	11.75	.3482	1.74
1 hr	.6284	.3317	.0028	.0154	.9537	.3654	11.81	.3946	----------
2 hr	.7624	.3095	.0008	.0102	.9617	.5257	11.94	.5452	----------
8 hr	1.6125	.1538	.0025	.0020	.9850	--------	12.33	1.5035	----------

To determine the amount of lime combined with silica in these solutions it was assumed that the sulphate was present as calcium sulphate and alumina as monocalcium aluminate.[48] The dissolved alumina is so low that even if it were not so combined in the presence of calcium sulphate the calculation would not be seriously in error. Electrometric measurements were made of the quantity of uncombined calcium hydroxide in these solutions. The lime in solution in excess of that required to form calcium sulphate and monocalcium aluminate and not present as free calcium hydroxide was calculated as combined with silica (column 10). The good agreement between these molar ratios of combined lime to silica and previous determinations at corresponding lime concentrations indicates that the particular part of the reaction between portland cement and water involving anhydrous calcium silicates is not essentially different from the reactions of the individual constituents, $3CaO \cdot SiO_2$ and β–$2CaO \cdot SiO_2$, with water. The solutions derived from the cement were also metastable and gave hydrated precipitates similar to those obtained from other unstable lime-silica solutions.

To determine whether or not the presence of calcium sulphate had any appreciable effect upon the rate of hydrolysis of β–$2CaO \cdot SiO_2$ and $3CaO \cdot SiO_2$, these compounds were shaken with a solution of approximately the same calcium sulphate content as that formed during the earlier periods in the reaction between water and the portland cement. From figure 6, where lime in excess of calcium sulphate is plotted against silica in solution, it is seen that the calcium sulphate, at the concentration present, retards the reaction but little.

[48] See footnote 6, p. 754.

The sulphate concentration of the original solution was practically unchanged after contact with the calcium silicate, differing in this respect from the reaction of water on the portland cement which contained both aluminates and silicates. Values were obtained for the molar ratios of combined lime to total silica in solution upon the assumption that the total lime less the sum of that present as free calcium hydroxide and combined as calcium sulphate represented lime combined with silica. The good agreement of the molar ratios with those previously obtained at corresponding lime concentrations and the fact that decomposition of these solutions, which were supersaturated in silica, did not appreciably alter the sulphate concentration indicates the correctness of the assumption that calcium sulphate is present uncombined in solution.

Insofar as the calcium silicates are concerned, therefore, the reaction of portland cement with water appears to involve the formation of supersaturated solutions of calcium silicate and subsequently of calcium hydroxide and spontaneous precipitation from such solutions. The results indicate that hydrated calcium orthosilicate, $Ca_2SiO_4 \cdot nH_2O$, together with solid calcium hydroxide are products of the reaction of portland cement with water under usual conditions, the hydrolysis of the former compound being reduced by the supersaturated solution of calcium hydroxide which is formed. Such a process, involving the formation of supersaturated solutions from the anhydrous compounds and the spontaneous precipitation of much less soluble products therefrom, is in agreement with the mechanism of hydraulic reactions first proposed by Le Chatelier.[49] The subsequent setting and hardening may then occur through the withdrawal of water from the hydrated products according to the mechanism suggested by Michaelis.[50]

If, in these experiments, the calcium silicates had been treated with a quantity of water similar to that used in the technical cement mix it is believed that the resultant products would not be essentially altered since only a relatively small quantity of the anhydrous calcium silicate is required to form the solution supersaturated with respect to calcium hydroxide with which the final hydrated silicate may exist in equilibrium. It may be definitely concluded from the results of this investigation that the calcium silicates occurring in cement are not hydrolyzed completely to silicic acid and calcium hydroxide in the presence of a relatively small quantity of water, as has sometimes been stated. Such extensive hydrolysis can occur only when the lime concentration has been reduced to a few hundredths of a gram of CaO per liter, a condition not likely to occur in the setting of portland cement. Instead, hydrated calcium orthosilicate and calcium hydroxide appear to be the most probable products of the reaction under usual conditions.

The influence of alkalies, which are nearly always present in cement, and of sulphate in higher concentrations than those studied in this paper as well as the nature of products, other than hydrated calcium silicate and calcium hydroxide, which may be formed during the reaction of portland cement with water, are not considered in this study.

[49] See footnote 3, p. 752.

[50] See footnote 7, p. 757.

V. REACTIONS OF DIATOMACEOUS SILICA AND OF SILICA GEL WITH LIME SOLUTION

A reactive naturally occurring form of silica is diatomaceous silica. The pozzolanic properties of this material are apparently due to its capacity to fix lime in chemical combination in the presence of water giving hydrated calcium silicate which is capable of setting and hardening. The reaction is essentially the reverse of that which occurs between the anhydrous calcium silicates and water but the composition of the final products should also be governed by the equilibrium relationships in the system $CaO–SiO_2–H_2O$ as shown in figure 9. It was decided to include some phases of an investigation of the reaction between diatomaceous silica and lime solution in this study, which chronologically had been completed before the present investigation was started.

The only report of the previous study was that briefly described in B.S. Technical News Bulletins nos. 141 and 142 (January and February 1929, respectively). It is believed that some of the unpublished results are now clarified by the present information on the system $CaO–SiO_2–H_2O$.

The method was similar in principle to that developed at the Building Research Station of Great Britain [51] for evaluating the pozzolanic activity of a material in that it involved the measurement of the rate of change in concentration of calcium hydroxide in solutions in contact with the pozzolana. The present procedure was to place weighed quantities (1.0 g) of the diatomaceous silicas and measured volumes (250 ml) of saturated lime solution (1.15 g CaO per l) in flasks which were then stoppered tightly and shaken at frequent intervals. After definite periods of time the solutions were filtered from the solid residues and their lime concentrations determined by titration with standard hydrochloric acid. Fifteen commercial diatomaceous silicas and 3 other forms of finely divided silica were studied, 8 initial mixtures of each being made up and allowed to stand for various lengths of time.

It was found that the reaction of all the diatomaceous silicas was very similar: First a rapid decrease in lime content of solutions occurred, followed by a more gradual reduction in the lime concentration until a rather definite final value of 0.07–0.09 g CaO per liter was reached. This limiting concentration was apparently not greatly altered by 4 years' contact between the solid phase and solution.

The other forms of silica included a microcrystalline mineral silica, an amorphous silica, and ground quartz (100 percent through a no. 200 sieve). These reduced the lime concentration of the solution after 4 years to 0.3880, 0.4630, and 0.6750 g CaO per liter, respectively.

To determine whether the decrease in lime concentration was attended by a simultaneous increase in the concentration of silica in solution, the series illustrated in figure 8, curve A, was prepared. This series consisted of 11 mixtures of a diatomaceous silica and lime solution which were allowed to stand for various lengths of time, filtered, and analyzed for both lime and silica. The rate of removal of lime from solution by this diatomaceous silica is typical of the group

[51] A. D. Cowper and F. L. Brady, Pozzolanas, Building Research Bulletin No. 2 (Great Britain); Reports of the Building Research Board (of Great Britain) for the years 1926 to 1928, inclusive.

studied. Inspection of the figure shows that with the lime concentration reduced to approximately 0.1 g CaO per liter a very sharp increase in silica concentration occurred. Subsequently the lime concentration did not decrease greatly. The point corresponding to the highest silica concentration represents a solution obtained after 4 years' contact with the diatomaceous earth.

Estimations were also made of the extent of combination of lime and silica in the residue by analyzing the portion soluble in 10 percent HCl at various stages of the reaction. It was found that the molar ratios of lime to silica in the soluble portion were approximately the

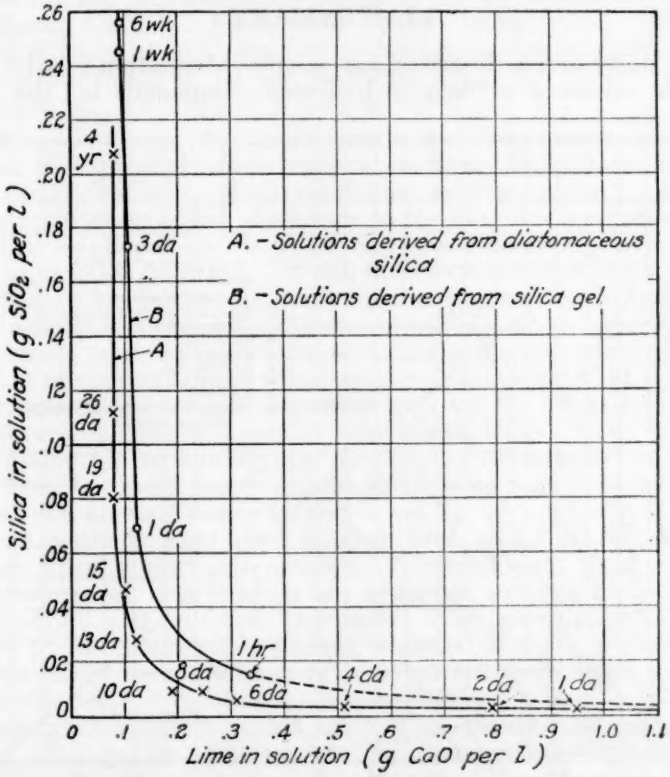

FIGURE 8.—*Showing the compositions of solutions resulting after increasing time of contact between (A) a diatomaceous silica and lime solution, and (B) silica gel and lime solution.*

same as those shown in figure 9 at corresponding lime concentrations. Thus it appears that initially small amounts of the more basic calcium silicates are formed but as the lime concentration decreases the molar ratio of combined lime to silica in the solid phase also decreases. As the reaction proceeds, more and more lime is taken up in chemical combination by the silica until the solid phase approaches equilibrium with the solution.

Curve B, figure 8, compares the reaction of the silica gel used in this study with that of the diatomaceous silica. The same proportion of silica to lime solution of corresponding initial concentration was

V. REACTIONS OF DIATOMACEOUS SILICA AND OF SILICA GEL WITH LIME SOLUTION

A reactive naturally occurring form of silica is diatomaceous silica. The pozzolanic properties of this material are apparently due to its capacity to fix lime in chemical combination in the presence of water giving hydrated calcium silicate which is capable of setting and hardening. The reaction is essentially the reverse of that which occurs between the anhydrous calcium silicates and water but the composition of the final products should also be governed by the equilibrium relationships in the system $CaO–SiO_2–H_2O$ as shown in figure 9. It was decided to include some phases of an investigation of the reaction between diatomaceous silica and lime solution in this study, which chronologically had been completed before the present investigation was started.

The only report of the previous study was that briefly described in B.S. Technical News Bulletins nos. 141 and 142 (January and February 1929, respectively). It is believed that some of the unpublished results are now clarified by the present information on the system $CaO–SiO_2–H_2O$.

The method was similar in principle to that developed at the Building Research Station of Great Britain [51] for evaluating the pozzolanic activity of a material in that it involved the measurement of the rate of change in concentration of calcium hydroxide in solutions in contact with the pozzolana. The present procedure was to place weighed quantities (1.0 g) of the diatomaceous silicas and measured volumes (250 ml) of saturated lime solution (1.15 g CaO per l) in flasks which were then stoppered tightly and shaken at frequent intervals. After definite periods of time the solutions were filtered from the solid residues and their lime concentrations determined by titration with standard hydrochloric acid. Fifteen commercial diatomaceous silicas and 3 other forms of finely divided silica were studied, 8 initial mixtures of each being made up and allowed to stand for various lengths of time.

It was found that the reaction of all the diatomaceous silicas was very similar: First a rapid decrease in lime content of solutions occurred, followed by a more gradual reduction in the lime concentration until a rather definite final value of 0.07–0.09 g CaO per liter was reached. This limiting concentration was apparently not greatly altered by 4 years' contact between the solid phase and solution.

The other forms of silica included a microcrystalline mineral silica, an amorphous silica, and ground quartz (100 percent through a no. 200 sieve). These reduced the lime concentration of the solution after 4 years to 0.3880, 0.4630, and 0.6750 g CaO per liter, respectively.

To determine whether the decrease in lime concentration was attended by a simultaneous increase in the concentration of silica in solution, the series illustrated in figure 8, curve A, was prepared. This series consisted of 11 mixtures of a diatomaceous silica and lime solution which were allowed to stand for various lengths of time, filtered, and analyzed for both lime and silica. The rate of removal of lime from solution by this diatomaceous silica is typical of the group

[51] A. D. Cowper and F. L. Brady, Pozzolanas, Building Research Bulletin No. 2 (Great Britain); Reports of the Building Research Board (of Great Britain) for the years 1926 to 1928, inclusive.

studied. Inspection of the figure shows that with the lime concentration reduced to approximately 0.1 g CaO per liter a very sharp increase in silica concentration occurred. Subsequently the lime concentration did not decrease greatly. The point corresponding to the highest silica concentration represents a solution obtained after 4 years' contact with the diatomaceous earth.

Estimations were also made of the extent of combination of lime and silica in the residue by analyzing the portion soluble in 10 percent HCl at various stages of the reaction. It was found that the molar ratios of lime to silica in the soluble portion were approximately the

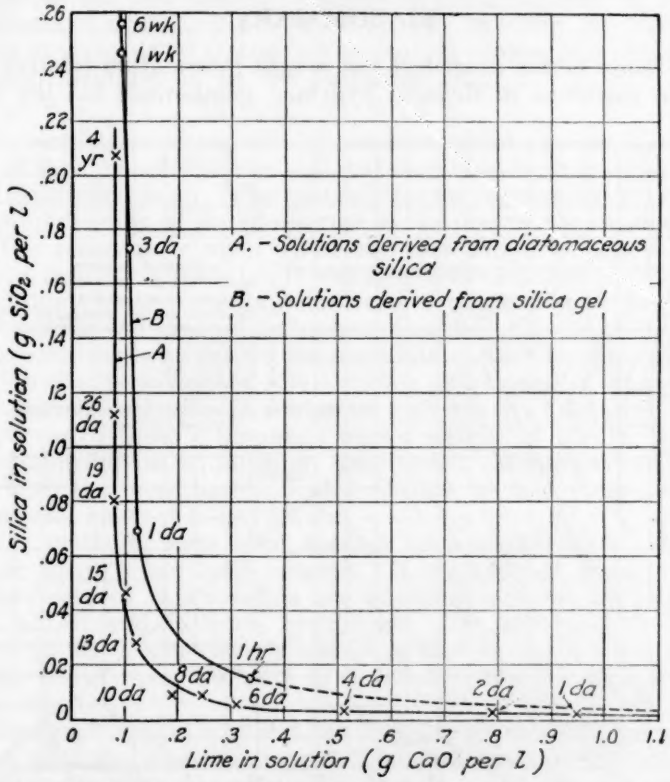

FIGURE 8.—*Showing the compositions of solutions resulting after increasing time of contact between (A) a diatomaceous silica and lime solution, and (B) silica gel and lime solution.*

same as those shown in figure 9 at corresponding lime concentrations. Thus it appears that initially small amounts of the more basic calcium silicates are formed but as the lime concentration decreases the molar ratio of combined lime to silica in the solid phase also decreases. As the reaction proceeds, more and more lime is taken up in chemical combination by the silica until the solid phase approaches equilibrium with the solution.

Curve B, figure 8, compares the reaction of the silica gel used in this study with that of the diatomaceous silica. The same proportion of silica to lime solution of corresponding initial concentration was

used in these experiments. It is seen that the silica gel is by far the more active, giving solutions containing appreciably higher concentrations of silica in much shorter periods of time. In the region of the equilibrium curve DE, figure 9, the rate of solution is strongly inhibited and the maximum solubility of silica, corresponding to point D was not attained. However, it is of interest that the compositions of the solutions follow the curve DE as the concentration of silica increases.

The lesser reactivity of the diatomaceous silica may be due to the presence of impurities and a coarser structure than that of the silica gel.

VI. SUMMARY

The study herein described has sought information relative to the possible existence of definite hydrated compounds in the system

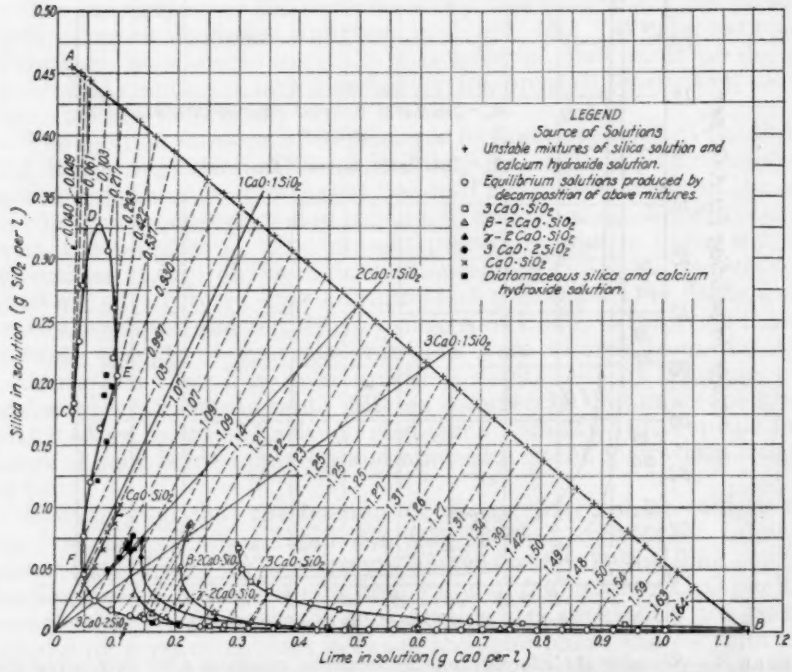

FIGURE 9.—*Comparison of solution and solid phase relationships in the system* $CaO–SiO_2–H_2O$ *with compositions of solutions resulting after increasing periods of contact between the anhydrous calcium silicates and water.*

$CaO–SiO_2–H_2O$ and their possible relationship to products formed by the reaction of water upon anhydrous calcium silicates. It did not include determinations of the extent of hydration of such compounds but attempted only to show that they are salts formed by the neutralization of a definite silicic acid by calcium hydroxide.

The sequence of procedure in this investigation was the following:

(1) The solubility relationships of lime and silica in solutions of increasing concentrations of lime up to saturation were investigated as well as the compositions of solid phases which could exist in

equilibrium with such solutions. These solid phases were amorphous or microcrystalline and could not be identified by petrographic methods.

(2) Electrometric measurements of the extent of combination of lime and silica in solution permitted the CaO/SiO_2 molar ratios found therein to be assigned to definite calcium silicates derived from orthosilicic acid and having the following formulas: $Ca(H_3SiO_4)_2$, CaH_2SiO_4, $Ca_3(HSiO_4)_2$, and Ca_2SiO_4. It proved to be possible to express the hydrolytic equilibria of these compounds in terms of the law of mass action and hydrolysis constants were calculated from the data for the four successive stages in the hydrolysis of calcium orthosilicate, Ca_2SiO_4. From these values, knowing the ionization constant of water at 30 C, the four ionization constants of orthosilicic acid were calculated to be the following: $K_{a_1}=2.2 \times 10^{-10}$, $K_{a_2}=2.0 \times 10^{-12}$, $K_{a_3}=1 \times 10^{-12}$, $K_{a_4}=1 \times 10^{-12}$.

(3) A correlation of the results obtained under (1) and (2) above, indicated that the solid phases in this system may be hydrated calcium salts of orthosilicic acid. Their solubilities are represented graphically and the application of the phase rule to the diagram is considered.

(4) The reaction between water and the anhydrous calcium silicates was then investigated. It was demonstrated that the solutions of compounds having the lime-silica molar ratios, 3:2, 2:1, and 3:1 are metastable and precipitate hydrated calcium silicate on standing. These results further support the postulate of Le Chatelier that the formation of supersaturated solutions is a characteristic phenomenon in the reactions of hydraulic materials with water. Metastable solubility curves of these compounds were constructed (fig. 9) to show their relationship to equilibrium conditions. Monocalcium silicate differs from the more basic calcium silicates in that it forms stable solutions and hence is nonhydraulic.

Similar methods were then applied to a study of the reaction of water upon a portland cement. It was found that probable solid products of this reaction are hydrated calcium orthosilicate, $Ca_2SiO_4 \cdot nH_2O$, and calcium hydroxide. The presence of calcium sulphate in the concentration used appears to have a practically negligible effect upon the rate of reaction between water and the calcium silicates.

(5) An investigation was also made of the reaction between diatomaceous silica and lime solution, and between silica gel and lime solution, which are in some respects the reverse of the reaction of water upon anhydrous calcium silicates.

WASHINGTON, March 22, 1934.

U.S. Department of Commerce Bureau of Standards

RESEARCH PAPER RP688

Part of Bureau of Standards Journal of Research, vol. 12, June 1934

PREECE TEST (COPPER-SULPHATE DIP) FOR ZINC COATINGS

E. C. Groesbeck and H. H. Walkup

ABSTRACT

The Preece test is in common use for inspection purposes to determine the uniformity of galvanized coatings, even though the results are sometimes erratic. An experimental study made with wires with different types of zinc coating and with wires consisting of commercially pure zinc and iron indicates that the pH value of the copper sulphate solution, the rate of solution of the zinc coating, and the cleanness of the test specimens are important factors in the Preece test. The use of cupric hydroxide instead of cupric oxide for neutralizing the copper sulphate solution is recommended, since a stable pH is much more quickly reached by its use. Electroplated and sprayed zinc coatings dissolve more rapidly in the copper sulphate solution than do hot-dipped or galvannealed coatings. Pure zinc coatings showed, during their solution, a "potential minimum" (with respect to a copper wire) which was practically absent with coatings that contain iron, such as on galvannealed wires and the inner layer of hot-dipped galvanized wires. This minimum may be caused by the delayed coagulation of basic zinc compounds which coagulation may be accelerated by the presence of iron. The causes and remedies of premature and delayed endpoints are explained. A method for measuring the thickness-distribution of the zinc coating by the use of a suitably acidified copper sulphate solution is suggested.

CONTENTS

	Page
I. Introduction	786
II. Preece test	786
1. Regular procedure	786
2. Difficulties encountered	787
3. Principle of the method	787
III. Experiments	788
1. Materials used	788
2. Factors that may affect the results	788
(a) Rate of solution of the coating	788
(1) Composition of copper sulphate solution	789
(2) Temperature	790
(3) Stirring	791
(4) Coating tested	791
Preparation	791
Composition and structure	792
(b) Premature endpoints	793
(1) Plastic films	793
(2) Potential measurements	794
(3) Oxygen concentration cells	798
(c) Delayed endpoints	799
(1) Adherence of copper	799
Effects of time and pH	799
Effects of composition and temperature	800
Use of bare steel as endpoint	800
(d) Distribution of thickness	800
IV. Conclusions	801
V. Selected references	802

I. INTRODUCTION

Zinc coatings find wide use for protecting iron and steel against corrosion, because zinc is more readily corroded than iron when they form a "couple" or electrolytic cell in the presence of a conducting liquid. In such a cell the zinc is the anode or dissolving electrode. Since this method of protection depends upon the protective value of the gradual corrosion of the zinc the protective value of the zinc coating depends primarily on its thickness at the thinnest spot.

The total weight or average thickness of a zinc coating is determined by some sort of a stripping method. A common stripping method consists in the removal of the coating by hydrochloric acid containing antimony chloride. If a determination of the distribution of the coating and its minimum thickness is desired, use may be made of a solution that will dissolve the zinc coating at a uniform rate and will reveal the base metal (iron) as soon as it is exposed. A copper sulphate solution of definite concentration is widely used commercially for this purpose in the procedure known as the "Preece test" (1).[1] Although this test is useful, experience has shown that the results are not always reproducible and consistent, (2), (3), (4), (5), especially when different types of zinc coatings are tested.

The experiments reported in this paper were made to determine relationships rather than to secure absolute data. This policy was prompted by a desire to establish the cause and possible remedies for the observed difficulties rather than the degree of error produced by any one variable.

II. PREECE TEST

1. REGULAR PROCEDURE

The Preece test is applied by dipping the zinc-coated article, which has previously been cleaned from grease or other foreign material, into a "neutral" solution of copper sulphate of a specified concentration (1.27 mole). This concentration is usually defined by its specific gravity (1.186 at 18 C), and the solution is maintained at a temperature of 18 C during the test. (6) The sample is immersed in the solution for 1 minute, removed, washed in running water, and freed from the loosely precipitated copper by light rubbing. The 1-minute immersions and cleanings are repeated until an endpoint is obtained in the form of a bright adherent deposit of copper. This indicates that the iron has been exposed there. The number of immersions (dips) reported for each sample is one less than that required for the appearance of adherent copper.

The use of this test in specifications rests on three assumptions: (a) The zinc coating dissolves at a uniform rate; (b) adherent copper is deposited as soon as the underlying iron is exposed; and (c) no adherent copper appears until the zinc coating is entirely removed at that point. Under such conditions the ability to withstand a specified number of immersions is evidence that the zinc coating possesses a certain minimum thickness.

[1] Figures in parentheses here and throughout the text refer to the numbers used in the list of references at the end of this publication.

2. DIFFICULTIES ENCOUNTERED

Practically, these criteria are approximately met by pure zinc coatings, such as those produced by plating, and fairly well by hot-dipped galvanized coatings. However, with coatings produced by "galvannealing" [2] or by sherardizing [3] the results are less consistent and are not always proportional to the thickness of the coatings. Such discrepancies may be the result of (a) differences in the rate of solution of the zinc coatings, (b) the formation of adherent copper before the zinc coating is all dissolved at that point—that is, a premature endpoint, or (c) the absence of adherent copper on iron that is exposed—that is, a delayed endpoint.

3. PRINCIPLE OF THE METHOD

At first glance, it may appear that the method depends merely on the displacement of copper by zinc, according to the reaction.

$$[1]\ Zn + CuSO_4 = Cu + ZnSO_4$$

This reaction, however, does not account for the deposition of adherent copper on the exposed iron rather than on the undissolved zinc.

It is much more probable that the reaction is electrolytic—that is, solution of zinc occurs at one point comprising an anode, with the deposition of copper at another point serving as a cathode. The cell may then be written:

$$[2]\ Zn\ (anode) \mid CuSO_4 \mid Cu\ (cathode)$$
$$\text{or } [3]\ Zn \mid Cu^{++} \mid Cu$$

This formula represents the system before any reaction occurs. However, after any finite period some zinc is in the solution adjacent to the zinc surface, and the cell is then represented by

$$[4]\ Zn \mid ZnSO_4 \mid CuSO_4 \mid Cu$$
$$\text{or } [5]\ Zn \mid Zn^{++} \mid Cu^{++} \mid Cu$$

In any case, the chemical reaction is

$$[6]\ Zn + Cu^{++} = Zn^{++} + Cu$$

To produce an electrolytic action, there must be a difference in potential between the two points which become, respectively, anode and cathode. This difference may arise from various causes and differences in the composition or temperature of the adjacent solution. According to this theory, a homogeneous piece of pure zinc will not react with a homogeneous solution of copper sulphate (just as very pure zinc dissolves very slowly in pure sulphuric acid).

The fact that a portion of a zinc specimen or of the zinc coating on steel does replace copper from a copper sulphate solution at once upon immersion is evidence that small areas of the zinc have slightly more positive single potentials than other areas, which latter serve as cathodes upon which the copper is deposited by the dissolving of the adjacent anodic areas. As soon as any copper is deposited, however, it serves as a cathode to the adjacent zinc, and the latter

[2] A proprietary process, in which the article (usually wire) is first coated with zinc by hot-dipping and is then heated.

[3] A zinc cementation process, in which the article is coated by heating in contact with powdered zinc.

dissolves with an accompanying precipitation of copper on the already deposited copper. This copper is nonadherent, since the surrounding and underlying zinc is continually dissolving. When a zinc coating on iron is completely dissolved at any point and the underlying iron is thereby exposed, the latter serves as a cathode to the surrounding zinc. An adherent deposit of copper is produced and constitutes the true endpoint. It should be noted that the production of adherent copper on the iron requires the presence of zinc adjacent to it. If a clean piece of iron is dipped into a neutral copper sulphate solution, the deposited copper is not very adherent, though usually more so than is copper deposited directly on zinc.

III. EXPERIMENTS

1. MATERIALS USED

Although committee A–5 of the American Society for Testing Materials expressed the opinion that the Preece test is unreliable and should be abandoned as a basis of specifications for galvanized sheet and plate, it admitted that this test is a quick and simple method for inspecting galvanized wire, for which it gives comparable results if properly applied (4). Since galvanized wire and wire products are important, wires with various types of zinc coatings were used in this study.

Wires coated with zinc by the hot-dip galvanizing, galvannealing, and electroplating (electrogalvanizing) processes were obtained from certain manufacturers. Two lots of hot-dipped galvanized wire from different sources (designated as c and k) were used. The electroplated wires were plated in a highly acid bath at a high-current density (about 750 amperes per square foot) with insoluble anodes. Wires were coated with zinc by metal spraying in the laboratory. As sherardizing is not commercially applied to wire, this type of coating was not included. Soft steel and commercially pure iron and zinc in wire form were used in the study of the effects of certain factors. The history of the iron, steel, and zinc wires is not known. The test specimens were generally about 3 inches (7.5 cm) long and ⅛ inch (3 mm) in diameter.

The term "Preece solution" used throughout the text refers to a copper sulphate solution of the concentration specified by the American Society for Testing Materials (6) regardless of its other characteristics, such as pH.

2. FACTORS THAT MAY AFFECT THE RESULTS

With the above theory as a basis, an effort was made to predict and to test the major effects of variations in operating conditions upon the time of formation, physical properties, and adherence on steel of the precipitated copper.

(a) RATE OF SOLUTION OF THE ZINC COATING

The use of the Preece test is generally based upon the assumption that the rate of solution of the zinc in various galvanized materials is practically the same. But this rate of solution depends upon 1, the composition of the copper sulphate solution; 2, its tempera-

ture; 3, the stirring; and 4, the composition and structure of the zinc coating, including any surface films that may be present initially or that formed during the reaction.

(1) COMPOSITION OF COPPER SULPHATE SOLUTION

The solution generally employed has a specific gravity of 1.186 at 18 C (6), which corresponds to a concentration of 1.27 mole or 315 g/l of $CuSO_4 \cdot 5H_2O$. Although this concentration is artibrary, it is not very critical, and hence no exhaustive tests were made on the effect of concentration on the rate of solution of the zinc. In general, an increase in copper content accelerates the solution of the zinc, and vice versa. The practical significance of this effect is that only a limited amount of a zinc coating should be tested in a given volume of copper sulphate solution, because the precipitation of copper reduces the concentration of copper sulphate.

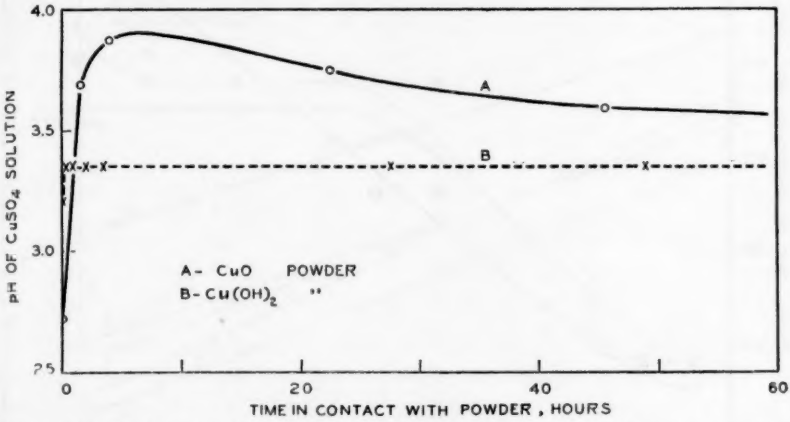

FIGURE 1.—*Change in* pH *value of the Preece solution with different neutralizing agents on standing.*

The neutralizing agents were added to portions of an unneutralized Preece test solution and the pH value was determined at intervals.

The neutral solution specified in the test is generally obtained by treating the solution of the salt with an excess of cupric oxide at room temperature. Small variations in acidity are most conveniently expressed in terms of hydrogen-ion concentration or pH. A neutral solution of copper sulphate is "acid" because of hydrolysis—that is, it has a pH less than 7, the neutral point of water. No published data could be found on the exact pH of copper sulphate solutions of about the concentration used in this work. However, the results of numerous measurements made with a quinhydrone electrode show that the equilibrium pH is about 3.3, which defines a truly neutral solution of copper sulphate.

The addition of finely divided cupric oxide to a copper sulphate solution with a pH of about 2.7 was found to raise the pH to nearly 4 in a short time (fig. 1). The pH then decreased to 3.3 on long standing (6 weeks) and an insoluble substance, believed to contain basic cupric sulphates (7), (8), was precipitated. It is evident that the final pH is the result of an equilibrium of sulphuric acid with

cupric hydroxide or basic cupric sulphate and not with cupric oxide. It is surprising that cupric oxide, which is not easily soluble, would have "over-neutralized" the solution. The use of basic cupric carbonate in place of cupric oxide gave similar results. On the other hand, cupric hydroxide very rapidly produced a pH value of about 3.3, which remained constant for a long period (fig. 1). The use of either powdered copper hydroxide or basic copper carbonate has been previously recommended for neutralizing purposes. (9)

Since, as will be shown, the pH of the solution affects the results, it is important to reach the desired pH quickly and to maintain it during the test. The substitution of cupric hydroxide for cupric oxide

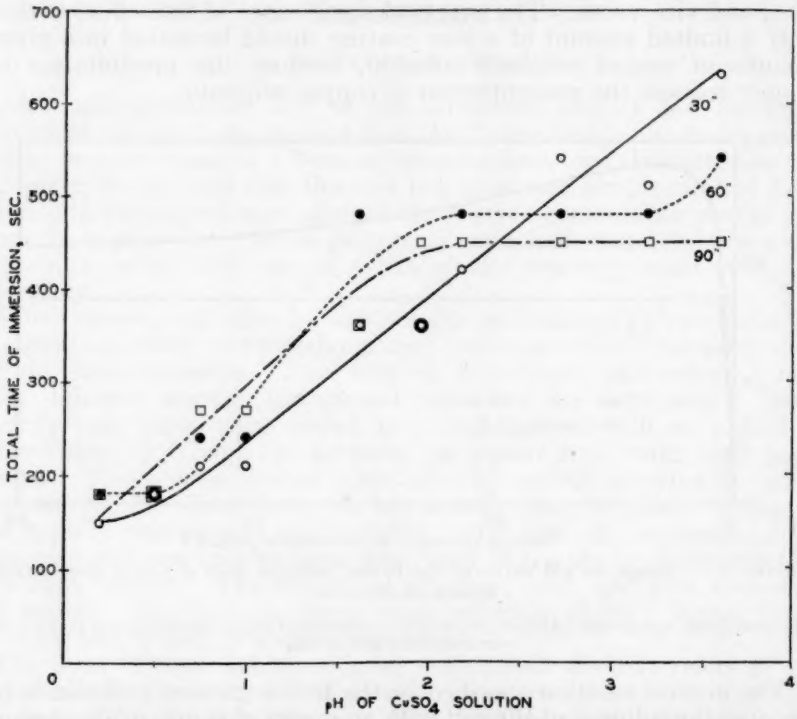

FIGURE 2.—*Effect of* pH *on the rate of solution of a galvannealed coating.*

In each experiment the coated wire was subjected to the Preece solution at about 20 C for successive periods of 30, 60, or 90 seconds, respectively, until a true endpoint was obtained. The pH of the solution was varied by suitable additions of H_2SO_4. The specimens were cleaned with tap water and a dry towel after each immersion.

in neutralizing the solution appears very desirable. As noted above, pH values greater than 3.3 may be obtained with cupric oxide or carbonate, but such solutions are unstable. For experimental purposes, sulphuric acid may be added to produce pH values below 3.3, which can conveniently be measured with a quinhydrone electrode. The rate of solution of the zinc was generally accelerated (fig. 2), by increasing the acidity (decreasing the pH) of the solution.

(2) TEMPERATURE

The rate of solution was found to increase, as expected, with the temperature (fig. 3). The reproducibility of these data does not

warrant the computation of exact temperature coefficients, but they show that the rate of solution is doubled by an increase of about 15 C. This indicates that to obtain an accuracy of about 10 percent in the Preece test it is necessary to keep the temperature constant (for example, at 18 C) within 2°.

(3) STIRRING

Moving the specimen, or agitating the solution, has the same effect as increasing the concentration of copper sulphate or of sulphuric acid, because stirring replenishes these compounds close to the metal surface. As it is impracticable to define a rate of agitation, especially for different shapes, it is desirable to avoid any agitation.

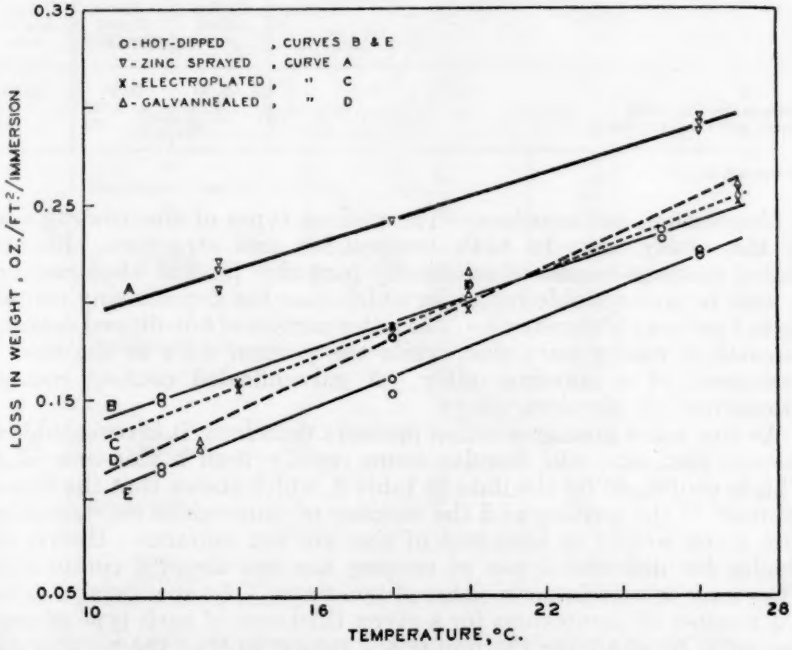

FIGURE 3.—*Effect of temperature of solution on average loss in weight for each immersion for different kinds of zinc coatings.*

(4) COATING TESTED

Preparation.—Obviously, any metal coating should be chemically clean when tested for its thickness or behavior. It is also obvious that the method of cleaning should be such that it does not remove any significant amount of the coating. Grease is best removed by an organic solvent, such as benzene, since alkaline solutions may attack the zinc. As it is not practicable to remove any oxide or carbonate films with acid, mechanical cleaning must be used. The data in table 1 indicate the greater rate of solution of zinc from a surface cleaned with fine emery paper (for example, aluminum oxide paper no. 400). The average amount of zinc removed by the emery paper was 0.04 oz/ft² with a maximum of 0.07 oz/ft². These losses represent not

more than 7 percent error in samples with coatings of 1.0 oz/ft² of the surface, but the error for thinner coatings would be correspondingly larger. It is thus evident that cleaning with even a fine abrasive, such as emery, must be done with great care.

TABLE 1.—*Effect of the initial cleaning method on the loss in weight during the first immersion*

[The solution was prepared by dissolving 36 g $CuSO_4 \cdot 5H_2O$ to 100 ml H_2O, and adding a slight excess of $Cu(OH)_2$. It was then shaken, let stand for 30 minutes and filtered. The temperature of the solution was approximately 20 C, and the immersion periods were 60 seconds]

Cleaning method	Loss in weight during first immersion		
	Electroplated wire	Hot-dipped wire (k) *	Galvannealed wire
	Oz/ft²	*Oz/ft²*	*Oz/ft²*
Benzene and dry towel	0.155	0.137	0.128
Emery paper and dry towel	.199	.165	.152

* See sec. III, 1.

Composition and structure.—The various types of zinc coating used in this study vary in both composition and structure. Electroplated coatings consist of practically pure zinc (except when mercury is used in zinc cyanide baths, in which case the deposit may contain up to 1 percent of mercury). The outer surface of hot-dipped coatings consists of nearly pure zinc, while the portion next to the steel is composed of a zinc-iron alloy. A galvannealed coating consists throughout of zinc-iron alloys.

As zinc has a greater solution pressure than iron, it is reasonable to assume that zinc will dissolve more rapidly than a zinc-iron alloy. This is confirmed by the data in table 2, which shows that the rate of solution of the coating and the number of immersions corresponding to a given weight or thickness of zinc are not uniform. Hence, the results for different types of coating are not directly comparable. They may be correlated in either of two ways: 1, by specifying a different number of immersions for a given thickness of each type of coating, or 2, by changing the immersion period so that the number will be the same for a given thickness. For example, if the period for electroplated coatings were retained at 60 seconds, the other periods would have to be approximately 55 seconds for zinc-sprayed, 80 seconds for hot-dipped, and 120 seconds for galvannealed. These figures are, however, not applicable in a practical way, because the weight of coating dissolved is not exactly proportional to the time. It is much simpler to use 60-second immersions and to specify the number of immersions that correspond approximately to any desired thickness of a given type of coating.

The initial increase in the solution rate reported for the hot-dipped specimens, followed by a decrease (table 2), is in agreement with Bablik's observation (5) that the solution rate for hot-dipped galvanized sheets increases at first and then decreases with continued immersions.

TABLE 2.—*Loss in weight of commercially pure zinc wire and of different types of zinc coating on iron wires for successive immersions in the Preece solution*

Material	Immersion number	Loss in weight	Average weight of coating, by stripping ($HCl-SbCl_3$)
		Oz/ft²	*Oz/ft²*
Zinc wire	1	0.170	
	2	.184	
	3	.186	
	4	.193	
	5	.163	
Total		.90	
Average		.18	
Electroplated wire	1	.155	1.32
	2	.247	
	3	.245	
	4	.226	
	5	.224	
	6	.215	
Total		1.31	
Average		.22	
Hot-dipped wire (k) [a]	1	.137	0.79
	2	.208	
	3	.168	
	4	.129	
Total		.64	
Average		.16	
Galvannealed wire	1	.128	1.04
	2	.106	
	3	.104	
	4	.110	
	5	.120	
	6	.112	
	7	.104	
	8	.108	
Total		.89	
Average		.11	
Zinc-sprayed	1	.243	[b] 1.17
	2	.251	
	3	.243	
	4	.220	
Total		.96	
Average		.24	

[a] See sec. III, 1.
[b] The weight of coating was determined by the difference in weight of the specimens before and after the metal-spraying process. Solution temperature and immersion periods as in table 1.

b. PREMATURE ENDPOINTS

(1) PLASTIC FILMS

Data on the rate of solution of zinc coatings are of practical value only if the endpoint can be reliably detected. The appearance of adherent copper on pure zinc coatings is usually definite and reproducible, but adherent copper sometimes appears on hot-dipped or galvannealed coatings before the coating has entirely dissolved underneath the copper deposit.

During cleaning, particles of precipitated copper may adhere to a zinc surface by being squeezed into recesses in a rough surface or into a plastic film, which may be formed during the reaction. The former result is unusual, but may occur if the pH value is very low (acidic), in which case the zinc is more violently attacked and consequently may be roughened. The occurrence of this latter result is favored by

conditions which permit the formation of basic precipitates on the zinc surface. The most obvious cause is too high a pH value of the solution. Under such conditions there will be a tendency for the precipitation of basic compounds from easily hydrolyzable salts. At the cathode of an electrolytic cell, the pH value tends to increase whenever hydrogen is evolved, a reaction that may occur when zinc is immersed in a copper sulphate solution which necessarily contains hydrogen ions. The hydrogen-ion concentration will also be reduced if any dissolved oxygen is electrolytically reduced on a cathodic area. Exact data are not available to permit the predication of the pH value at which basic compounds of copper, zinc, and iron may form in these solutions, especially as the respective concentrations of these metals are always changing.

If the copper sulphate is originally 1.27 mole, a complete reaction of this solution with the zinc coating should produce a zinc sulphate solution of the same molar concentration. Actually, some copper sulphate is always present in the solution adjacent to the zinc surface as a result of diffusion and convection. Furthermore, ferrous sulphate may be present in the portion of the solution next to the metal surface if the coating contains iron. The oxidation of the ferrous sulphate to the ferric condition would probably be prevented by the presence of zinc, although it may occur at a short distance from the metal surface. Therefore, the solution next to the metal contains, shortly after the immersion of the zinc-coated specimen, hydrogen, cupric, zinc, ferrous, and possibly ferric, ions. If, now, some of the hydrogen ions are removed, hydroxides (or basic salts) of copper, zinc or iron may be precipitated along with the metallic copper, and may cause the latter to adhere to the surface, even though no steel is exposed.

(2) POTENTIAL MEASUREMENTS

An effort was made to follow the course of the reaction when a zinc-coated specimen is immersed in a copper sulphate solution by making simple potential measurements in a cell consisting of (a) zinc or zinc-coated iron wire, (b) copper sulphate solution, and (c) copper wire. The total cell voltage was measured at intervals by means of a high resistance voltmeter.

When a zinc wire or a pure zinc coating (curve A, fig. 4) is immersed in the copper sulphate solution, there is a rapid decrease in potential to a sharp minimum, followed by a relatively slight rise, after which the potential decreases gradually. A potential-minimum was not observed in the case of galvannealed coatings.

There is no completely satisfactory explanation of a curve such as A. The potential measured is that of a primary cell such as the following:

Anode			Cathode
Zinc (or zinc coating)---	$ZnSO_4$ 0 to 1.27 mol	$CuSO_4$ 1.27 to 0 mol	Copper

As this cell is discharged, the concentration of zinc sulphate increases and that of copper sulphate decreases. Both of these changes cause a rapid decrease in cell potential, which is represented by the first, i.e., descending, portion of the curve.

If now the pH of the solution adjacent to cathodic areas increases, as explained above, there is a tendency for the formation of hydroxides or basic salts. At first these may be in colloidal solution and require a finite time for coagulation. If the latter occurs it would slow up the reaction, retard the precipitation of copper, and permit the original concentrations to be restored by diffusion or convection.

The absence of a potential minimum, when iron is present, may be an evidence that the iron compounds favor coagulation and thus prevent the "supersaturation" with basic compounds.

This explanation is consistent with curve B, which shows that the rate of reaction, i.e., the change in potential is at first rapid and then changes at a nearly uniform slower rate.

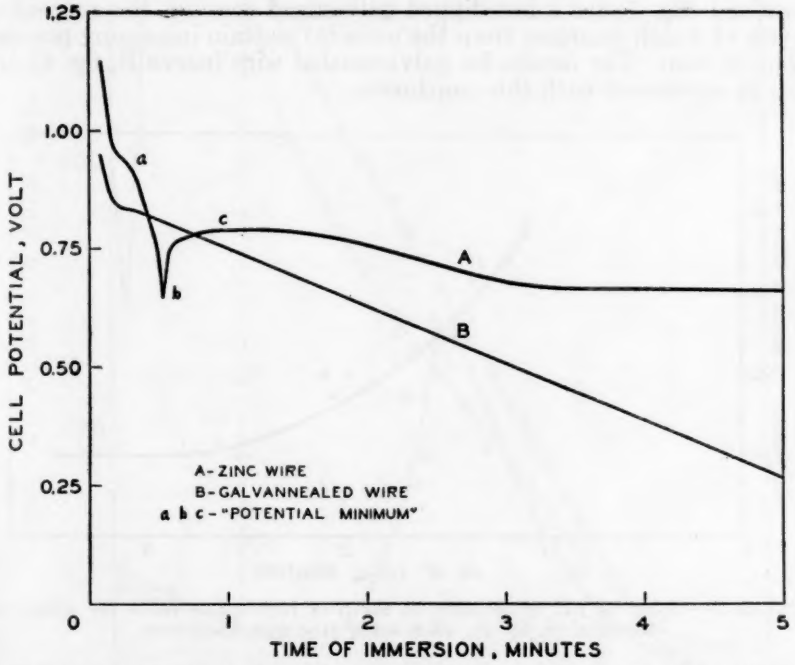

FIGURE 4.—*Change in potential with time of immersion for zinc wire and for galvannealed wire.*

The curves are representative of data obtained by using different galvanized and zinc wire specimens as the anode and various $CuSO_4$ solutions as the electrolyte in the cell, specimen | solution | copper wire, with the electrodes placed about 2 cm apart. A 25,000 ohm voltmeter, provided with a 0 to 2.5 volt scale, and a stopwatch were used.

A somewhat similar curve was obtained by Kreuchen (10) for the potential of a single zinc crystal in normal zinc sulphate solution. He reported that polycrystalline zinc showed a slightly higher potential without any such minimum and attributed the difference to the variation in solution pressure of zinc from a single complete crystal plane and from a broken surface. Such an explanation does not apply to the zinc coatings, which certainly are polycrystalline.

The effects of various factors upon the position of the potential minimum were next investigated. The time required to reach the minimum potential increased as the acidity of the copper sulphate

solution, which was at about 20 C, was increased (pH was decreased—fig. 5). If, as explained above, the occurrence of the minimum potential is related to the coagulation of hydroxides or basic salts in the copper sulphate solution, a decrease in the pH of the solution would increase the time needed for this coagulation to take place.

Figure 6 shows the effect of the temperature of the copper sulphate solution on the time required to reach the potential minimum. A satisfactory reason for the marked increase in the time, at 40 to 60 C, for zinc, and at lower temperature ranges for hot-dipped and galvannealed coatings, cannot be given, although the shifting of the peak in the curves to the left is apparently related to the iron content of the coating. That the presence of iron in the coating retards or prevents the occurrence of a potential minimum was confirmed by the results obtained (fig. 7) for a hot-dipped galvanized coating, the successive layers of which (starting from the outside) contain increasing proportions of iron. The results for galvannealed wire (curve B, fig. 4) are also in agreement with this conclusion.

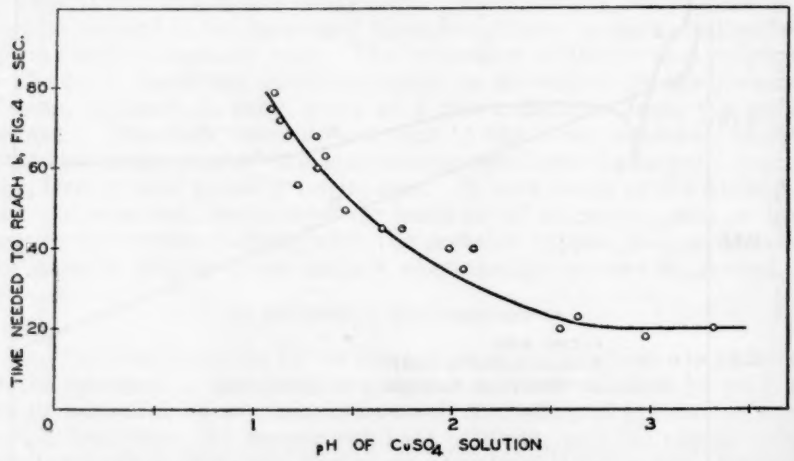

FIGURE 5.—*Effect of* pH *of solution on the time required to reach the minimum potential (b, fig. 4), when using zinc wire specimens.*

If then the basic films form more rapidly on the pure zinc than on the zinc-iron alloy, it is reasonable to suppose that the films formed on the latter would be more adherent and hence be more likely to retain copper particles after the cleaning operation.

That plastic material may be formed on the surface of the coatings, especially of zinc-iron alloys, was shown by numerous observations, summarized (a, b, c), as follows, in which the specimens were washed in running tap water and wiped dry with a towel after immersion in copper sulphate solution.

(*a*) A pure zinc wire acquired a dull color after a short immersion and a gray color after a period corresponding approximately to the minimum, b, in figure 4. A longer immersion produced a bright metallic luster, and little or no plastic material could be detected on the surface.

(*b*) A plastic film was left on hot-dipped galvanized wires, the amount of which increased with the greater iron content of the lower layers of the coating.

(*c*) Plastic material was found on the surface of the galvannealed wires.

No potentital minimum was observed when a zinc wire was immersed in a copper sulphate solution containing potassium dichromate, but the surface was coated with a black film. Immersion for a long

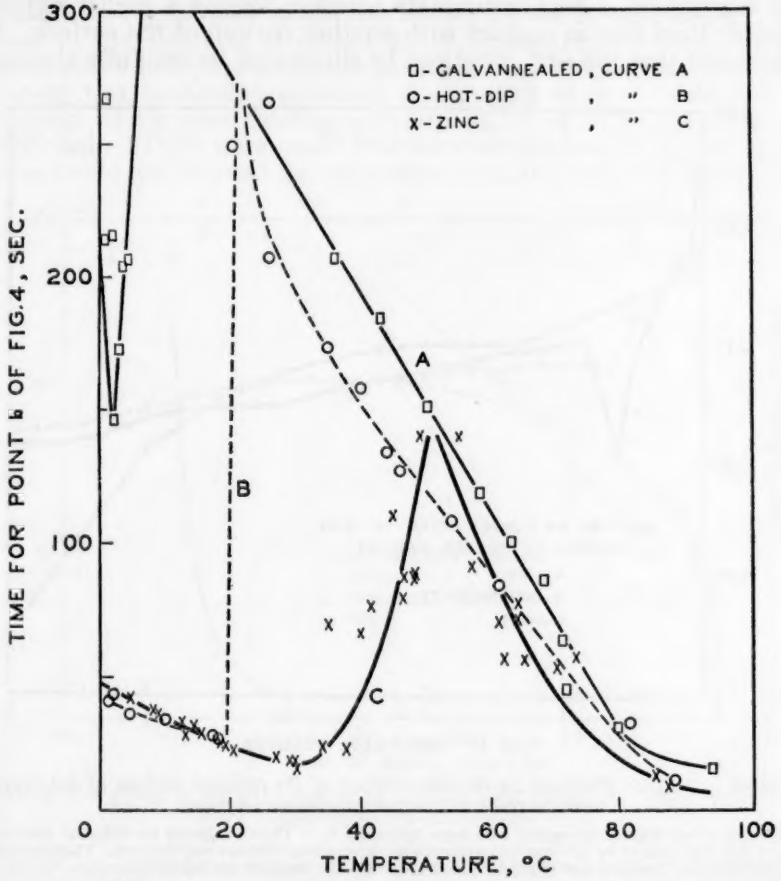

FIGURE 6.—*Effect of temperature of the* $CuSO_4$ *solution on the time required to reach the "potential minimum" (b, fig. 4).*

A Preece solution of pH 3 was used.

period produced a plastic residue, which contained a white gelatinous material (presumably basic zinc sulphate), metallic copper, and a black substance (probably containing copper oxide). The dichromate is an oxidizing agent that is readily reduced by zinc, and hence the pH of the solution was raised to a point where basic compounds were precipitated, as predicted above. It was found that by immersing galvannealed wires in a copper sulphate solution with a pH between 1

and 2 for periods of 120 seconds or more the tendency for the production of premature endpoints was decreased.

(3) OXYGEN CONCENTRATION CELLS

It was predicted that copper may deposit adherently on zinc surfaces if there is sufficient difference of potential to make certain areas cathodic. Such a condition may arise if a portion of the zinc surface is either (a) protected by a film that reduces its solution pressure, or (b) exposed to a copper sulphate solution having a higher oxygen content than that in contact with another portion of the surface. It was found that the first cause can be eliminated by carefully cleaning

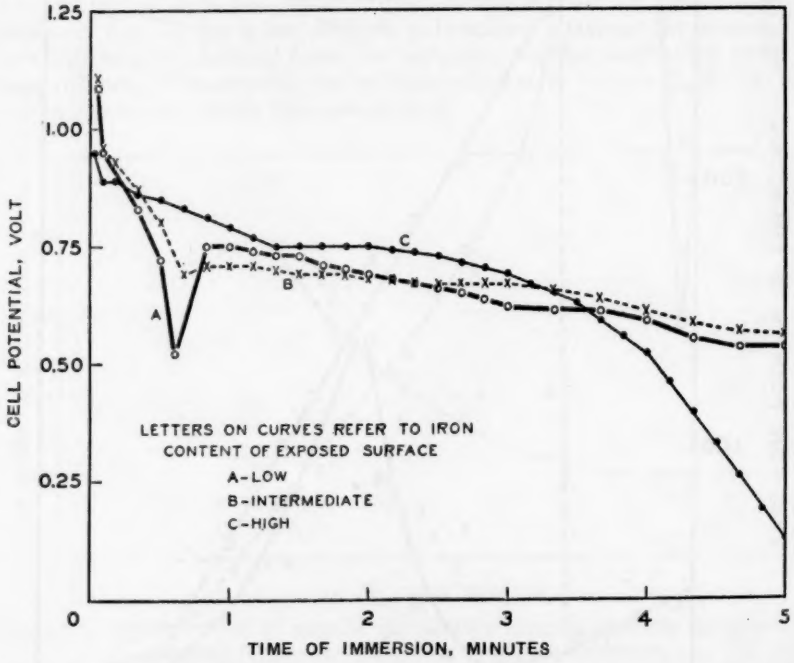

FIGURE 7.—*Effect produced by the iron content of the exposed surface of hot-dipped zinc coatings on the potential-time relation.*

Specimens of hot-dipped galvanized wire were immersed in a $CuSO_4$ solution for different periods of time and were cleaned by rubbing with a pencil eraser until a bright surface was obtained. They were then immersed in a Preece solution of pH 3.2 which was at 10 C for securing the data given.

the specimen before the first immersion and by rubbing it rather firmly between immersions, for example, with a soft pencil eraser.

The effect of an oxygen concentration cell is noticeable near the "water line" of the Preece solution, and it may be accentuated by rotating the partially immersed specimen eccentrically, whereby localized aeration is produced. If this effect is combined with local surface contamination, copper readily deposits on the uncleaned part of the surface. Agitation of the specimen in the Preece test should, therefore, be avoided.

If, for any reason, the zinc dissolves more rapidly at one point than at another, for example, at the water line or near previously exposed steel or abraded areas, copper will deposit on the steel there sooner

than at other points. Strictly speaking, this latter effect is not a premature endpoint, but is a true criterion of a defective coating. Such defects, if incidental to the preparation or testing of the specimens, should, of course, be disregarded.

(c) DELAYED ENDPOINTS

(1) ADHERENCE OF COPPER

Effects of time and pH.—If, for any reason, copper does not adhere to steel that is exposed in the test the result will be misleading. Because of the difficulty of measuring or expressing the degree of adherence, the following empirical procedure was employed. A copper coating was considered adherent to the steel when it could not be removed by vigorous rubbing with dry cotton or by flaking with the finger nail. Tests were made to determine the length of time specimens could be exposed to the copper sulphate solution before the

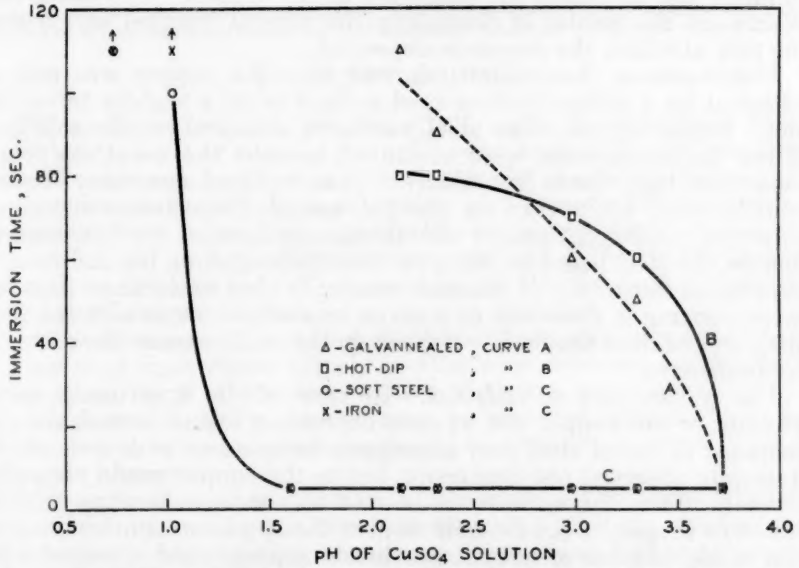

FIGURE 8.—*Effect of the* pH *value of the* $CuSO_4$ *solution on the "adherence time" of the copper deposited on iron and steel.*

copper deposit became detached from the iron or steel, which had been initially exposed by filing off a portion of the coating.

In the experiments reported in figure 8, several specimens of the same material were immersed for different periods, each specimen being used only once. The curves present the observed relations rather than the specific data. The specimens were cleaned by first rubbing with aluminum oxide paper no. 400 and then by immersing in a 10 percent H_2SO_4 solution for 5 to 10 seconds, followed by washing in water and wiping dry with a cotton swab. Immediately after drying, they were immersed in the $CuSO_4$ solution at 20 C. The degree of adherence subsequent to the immersion in $CuSO_4$ solution was approximately defined by the above rubbing and flaking tests.

In all cases the adherence of the copper decreased as the pH was increased (fig. 8), though it was adherent for approximately 1

minute when the pH was 3.3, the recommended value. On the other hand, the copper deposited on uncoated iron or steel wire was practically nonadherent if the pH was much above 1. (This agrees with the general use of an acidified copper sulphate solution to produce copper films on steel by immersion.)

It is of interest to note here that a "contrast in color" method is made use of in a Navy Department specification (11), in which a bright adherent copper deposit on steel is prepared each day of test as a standard color sample for comparison with the color of the copper deposits formed on galvanized wires in the Preece test.

Effects of composition and temperature.—Other tests showed that the adherence of the copper on the galvanized wires was decreased by very small concentrations of chloride or nitrate in the copper sulphate solution. The adherence was increased by cooling the solution, for example, from 30 to 5 C. A decrease in concentration of copper sulphate also increased the adherence of the copper. The latter two effects are the results of decreasing the rate of reaction and hence, the rate at which the copper is deposited.

Miscellaneous observations showed that the copper was not as adherent on a perfectly clean steel surface as on a slightly tarnished one. Evidently the clean steel was itself attacked by the solution. When the immersions were continued beyond the usual endpoint, the copper that was at first adherent on zinc-plated specimens became nonadherent, while that on the galvannealed specimens remained adherent. Adherent copper did not always form in the first immersion on the steel bared by filing an electroplated wire, but did in subsequent immersions. If the zinc coating is very uniform so that the entire coating is dissolved in a given immersion (especially the first one), copper does not readily deposit on the steel, even in the succeeding immersion.

Use of bare steel as endpoint.—In view of the uncertainty as to whether or not copper will at once deposit on exposed steel, the appearance of bared steel may sometimes serve as an endpoint, which is usually observed one immersion before the copper would normally deposit. Since the appearance of steel is not so evident as that of adherent copper, it is advisable to give the specimen another immersion to see whether or not the previously exposed steel is coated with adherent copper. In effect, this practice would not differ from the usual procedure, except that the appearance of steel would serve as a warning that the endpoint would probably occur on the next immersion.

(d) DISTRIBUTION OF THICKNESS

While the Preece test is commonly used merely to detect areas having a minimum thickness, it may be modified so as to give an approximate idea of the thickness distribution. This is accomplished by noting the relative areas coated with copper in immersions succeeding the endpoint. The neutral copper sulphate solution (pH–3.3) is not satisfactory for this purpose, since exposure to succeeding immersions causes the previously adherent copper to become detached. If, however, sufficient sulphuric acid is added to lower the pH to about 0.6, for example, 3 ml of concentrated H_2SO_4 to 100 ml of neutral $CuSO_4$, the copper deposit remains adherent throughout the successive immersions. The results (table 3) show that in these tests

the plated and galvannealed coatings were more uniform than the hot-dipped or sprayed ones.

TABLE 3.—*Proportion of area covered with adherent copper after successive immersions for 30-second periods*

Type of coating	Surface covered with deposited copper in immersion periods subsequent to the first appearance of bared steel					
	1	2	3	4	5	6
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
Electroplated	60	95	100			
Galvannealed	5	90	99			
Hot-dipped (k)[a]	2	90	95	99		
Hot-dipped (c)[a]	10	30	70	90	100	
Zinc-sprayed	5	40	60	90	99	99

[a] See sec. 3, 1.

Solution: 3 ml of concentrated H_2SO_4 were added to 100 ml of a solution that was prepared in the same way as for table 1; temperature of the solution, 18 C; concentration, 1.27 mol-$CuSO_4.5H_2O$; and pH, 0.65.

IV. CONCLUSIONS

1. If a copper sulphate solution (1.27 mole) is neutralized with cupric oxide, a pH of 4.0 may be rapidly obtained. On long standing the pH decreases to about 3.3, and a basic precipitate forms. A similar result is secured by neutralizing with basic cupric carbonate. Treatment with cupric hydroxide produces inside of 24 hours a solution with a pH of 3.3, which is permanent and probably represents the true equilibrium pH. The use of cupric hydroxide as a neutralizing agent is recommended.

2. The specimens to be tested should be thoroughly cleaned before and between immersions (dips), as otherwise adherent copper may form on portions of the zinc surface that are not entirely clean. Grease that is initially present may be removed with an organic solvent, while corrosion products should be carefully removed with a very mild abrasive.

3. The rate of solution of zinc coatings in copper sulphate solution is increased by raising the concentration of (a) copper sulphate or (b) free acid. Stirring also increases the rate of solution of the coating, and therefore should be avoided in the test. Adherent copper may form on zinc coatings if the wire specimens are rotated eccentrically, which probably produces oxygen concentration cells.

4. Electroplated and sprayed zinc coatings dissolve more rapidly than hot-dipped or galvannealed coatings. For a given thickness of coating, a greater number of 60-second immersions, or else longer immersions must, therefore, be specified for the latter two coatings.

5. The potential of zinc, or of a pure zinc coating, in a copper sulphate solution decreases rapidly for about one minute to a potential-minimum, then increases slightly, and finally gradually decreases. No such potential minimum is observed with galvannealed coatings or with the iron-rich layer of hot-dipped coatings. The minimum may be caused by the delayed coagulation of basic zinc compounds. The presence of iron may accelerate this coagulation to form a more dense film, that prevents such a minimum. The position of the potential minimum is affected by the pH and temperature of the copper sulphate solution.

6. Premature endpoints, that is, adherence of copper before the underlying steel is exposed, may be caused by the formation of plastic material on the metal surface during the test. This is more likely to occur with zinc coatings containing iron, such as galvannealed coatings or the inner layer of hot-dipped coatings. Its effect can be eliminated by a thorough rubbing of the dried specimen between immersions with a soft abrasive, for example, a pencil eraser.

7. Delayed endpoints may result from the failure of copper to deposit immediately on steel that is exposed. In such cases the appearance of the bare steel may serve as an approximate endpoint, which may usually be confirmed by the deposition of copper in the succeeding immersion.

8. The adherence of copper to the bare steel may be improved by lowering the pH, though it is usually adherent for at least 1 minute when the pH is 3.3.

9. By using a more acid solution, for example, pH = 0.6, successive immersions after the first appearance of adherent copper may be used to study the thickness distribution of the coating.

V. SELECTED REFERENCES

1. M. Pettenkofer, Ueber ein einfacher verfahren, die dicke einer verzinkung auf eisen zu schützen. München, Natl. Tech. Comm. Abh. I, p. 159, 1857.
2. W. A. Patrick and W. H. Walker, Method for testing galvanized iron to replace the Preece Test. Ind. Eng. Chem. vol. 3, p. 239, 1911.
3. W. M. Peirce, The Preece Test for zinc-coated materials. Iron Age, vol. 114, p. 199, 1924.
4. Report of Committee A–5 on Corrosion of Iron and Steel. Proceedings, Amer. Soc. Testing Matls., vol. 9, p. 100, 1911, and vol. 17, p. 144, 1917.
5. H. Bablik, The Preece Test. Metal Industry (London), vol. 28, p. 369, 1926.
6. Appendix to Standard Methods of determining weight of coating on zinc-coated articles: Preece or copper sulphate dip test. Amer. Soc. Testing Matls. Book of A.S.T.M. Standards, part I, p. 323, 1933.
7. S. W. Young and A. E. Stearn, The basic copper sulphates. J. Amer. Chem. Soc., vol. 38, p. 1947, 1916.
8. H. H. Walkup and E. C. Groesbeck, Some factors affecting the Preece Test for zinc coatings. Proc. Amer. Soc. Testing Matls., vol. 32, part II, p. 453, 1932.
9. British Standard Specification for the testing of the zinc coating on galvanized wires, Bull. no. 433, British Standards Institutions, London, 1932.
10. K. H. Kreuchen, Electrolytische untersuchungen an Zinkeinkristallen. Z. Physik. Chem., vol. 155, Abh. A,. p. 161, 1931.
11. United States Navy Department Specification (22–W–10a), dated June 1, 1932.

WASHINGTON, June 8, 1933.

U.S. DEPARTMENT OF COMMERCE BUREAU OF STANDARDS

RESEARCH PAPER RP689

Part of Bureau of Standards Journal of Research, vol. 12, June 1934

IODINE NUMBER OF WOOL: A METHOD FOR DETERMINING THE ACTION OF VARIOUS CHEMICAL REAGENTS ON WOOL AND OTHER PROTEINS

By Milton Harris, Harvey A. Neville, and William C. Fritz [1]

ABSTRACT

The purpose of this research was to find a method for determining the action of various chemical reagents upon wool. The iodine number provides a qualitative measure of the extent to which the amino groups are affected by various treatments of the protein.

Amino acids and proteins exhibit iodine numbers as determined by the standard method. The iodine numbers of such substances do not indicate ordinary unsaturation but are shown to be related to the free amino nitrogen content.

The iodine numbers of some typical proteins are reported and a general correspondence between the iodine numbers and the isoelectric points of the proteins is shown.

Conversion of amino groups to hydroxyl groups, combination of amino groups with strong acids, and other chemical reactions which affect the amino groups reduce the iodine numbers of amino acids (with the exception of cysteine) to zero.

Part of the iodine number of wool is shown to be due to cysteine which is very susceptible to oxidation. The iodine number of wool is therefore affected by reactions of chemical reagents with the amino or the cysteine groups.

This method will distinguish, for example, between reversibly adsorbed and chemically combined acid. The latter can be removed by the action of an alkali and this restores the original iodine number of the wool.

CONTENTS

	Page
I. Introduction	803
II. Methods	804
III. Results and discussion	805
1. Amino acids and derivatives	805
2. Proteins	806
3. Wool	807
IV. References	809

I. INTRODUCTION

The term "iodine number" is ordinarily associated with oils and fats for which it serves as a measure of chemical unsaturation. It represents the number of centigrams of iodine which combine with 1 gram of material.

[1] The experimental part of this research was done by William C. Fritz, Eavenson and Levering, Research Fellow at Lehigh University. The work was directed by Harvey A. Neville, Associate Professor of Chemistry at Lehigh University, and Milton Harris, Research Associate at the Bureau of Standards from the American Association of Textile Chemists and Colorists. The latter's contribution to this study forms a part of the study of wool being undertaken by the Association on a grant from the Textile Foundation.

The aliphatic amino acids are saturated compounds, but they nevertheless exhibit definite and reproducible iodine numbers which may be determined by the same methods as those used for fats and oils. The experimental evidence indicates that the iodine reacts only with the free amino groups in these compounds, unless, like cysteine, for example, they contain readily oxidizable groups which also react.

The iodine numbers of proteins may be determined by the same method used for oils and a part, at least, of the iodine number of each protein may be attributed to the free amino groups. This provides a useful means of determining the extent to which these groups are affected by various treatments of the protein.

This paper is a report of a brief survey on the use of this method for studying the action of various chemical reagents upon wool.

II. METHODS

The iodine numbers reported here were obtained by a slight modification of the standard Wijs method (1),[2] using a solution of iodine monochloride in glacial acetic acid, which was 0.1 normal with respect to total halogen. Samples of the amino acids or their derivatives weighing about 0.1 gram and of the proteins weighing about 0.5 gram were used for each determination.

The wool fibers were prepared by cutting them into very short lengths. The iodine number of the cut fibers was identical with that obtained from powdered wool. All samples were conditioned at a relative humidity of 65 percent (70 F). Conditioned and dried samples gave the same iodine number calculated on the basis of the wool protein.

The determinations of iodine numbers were carried out as follows: A weighed sample was placed in a flask and 25 ml of glacial acetic acid was added. Twenty-five ml of Wijs solution was added and the mixture was allowed to stand, with occasional shaking, for one half hour at 25 C. At the end of this time, 50 ml of water and 20 ml of a 15 percent solution of potassium iodide were added. Sodium thiosulfate solution was then added in an amount equal to that required by a blank determination. After the solution had stood for one half hour, 10 ml of a 1 percent starch solution was added and the excess of thiosulfate was titrated with a standard iodine solution. This modification, namely, the addition of excess thiosulfate and reverse titration with iodine, was used in all of the determinations of iodine numbers. By this procedure all of the iodine was removed from the wool fibers and the wool appeared as white as the original sample.

Analyses of wool samples which had been used for iodine number determinations showed that no chlorine or iodine remained in combination with the wool after the thiosulfate treatment. This indicates that the halogen which combined with the wool in the Wijs solution was removed by the aqueous solutions in some combined form and not as free iodine, since it did not react with its equivalent of thiosulfate.

[2] Figures in parentheses here and throughout the text refer to the references given at the end of this paper, page 809.

III. RESULTS AND DISCUSSION

1. AMINO ACIDS AND DERIVATIVES

The iodine numbers of a few amino acids and derivatives determined by the above method are recorded in table 1.

TABLE 1.—*Iodine numbers of a few amino acids and derivatives*

Compounds	Iodine number
Glycine – CH_2NH_2COOH	15.5
Glycollic acid – $CH_2OHCOOH$	0
Glycine hydrochloride – $CH_2NH_2COOH.HCl$	0
Leucine – $CH_3(CH_2)_2CHNH_2COOH$	20.6
Acetamide – CH_3CONH_2	0
Diethylformamide – $HCON-(C_1H_5)_2$	0
Urea – $CO(NH_2)_2$	0
Cysteine hydrochloride – $CH_2SHCHNH_2COOH.HCl$	89
Hippuric acid – $C_6H_5CONHCH_2COOH$	0

A simple amino acid such as glycine gives an iodine number while the corresponding hydroxy acid does not react with iodine and gives no iodine number. Further evidence that the iodine reacts only with the free amino group is offered by the fact that acid salts of the amino acids, such as the hydrochloride, likewise give no iodine number. However, the reaction of halogen with the simple amino acids is by no means complete under the conditions of these experiments since the theoretical iodine numbers of glycine and leucine, assuming a stoichiometric reaction, would be 338 and 194, respectively. It is obvious that the study of other factors such as pH values and molecular concentrations are necessary, if this method is to be made strictly quantitative. As the molecular weight of the amino acid increases, the reaction with iodine becomes more nearly complete and, as will be shown it is approximately stoichiometric for some of the proteins.

The hydrochloride of cysteine should give a zero iodine number if the reactions were limited to free amino groups. However, this particular amino acid contains the easily oxidizable –SH group which reacts with iodine to produce cysteine. The theoretical iodine number of cysteine hydrochloride corresponding to the reaction $2\ R.CH_2SH + I_2 = R.CH_2S–SCH_2.R + 2\ HI$ is 83. The value given in table 1 is in fairly good agreement in view of the difficulties attending the use of this reaction for the quantitative estimation of cysteine as reported by Lucas and King (2).

Since acetamide, hippuric acid, and similar amides give no iodine numbers, it may be concluded that the amide nitrogen does not contribute to the iodine number of a protein.

Reaction of iodine with the amino group may involve either an addition or an oxidation reaction. It may be assumed by analogy that the addition of iodine (or chlorine) from the Wijs solution occurs at the amino group in a manner similar to the addition of hydrochloric acid. The mode of combination of acids with amino groups has recently been discussed by Phillips (3), who represents the chlorine or other anion as bound to the molecule through an atom of hydrogen having four electrons in its shell. A similar structure may be used

to represent the combination of the amino group with two halogen atoms instead of with hydrochloric acid.

Since the Wijs solution is also an oxidizing agent, it is possible that the amino group has been at least partially oxidized during the iodine number determination (4).

2. PROTEINS

In table 2 are recorded the iodine numbers of some proteins. While it is not desired to place any emphasis upon iodine numbers as a means of comparing different proteins, a general relationship is evident.

TABLE 2.—*Iodine numbers and isoelectric points of a few proteins*

Protein	Source	Isoelectric point	Iodine number
Fibroin	Degummed silk	2.5 (5)	3.7
Keratin	Texas wool	3.4 (6)	14.2
Gelatin	Food	4.7 (7)	10.2
Zein	Corn	6.2 (8)	27.5
Gliadin	Wheat	6.5 (8)	25.0

Fibroin which has a low content of free amino nitrogen and an isoelectric point at a relatively high acidity, has a low iodine number. On the basis of isoelectric points and the accepted values for free amino nitrogen, wool keratin should be next in order with an iodine number less than that of gelatin. The apparent inconsistency in table 2 is readily explained by the fact that keratin is the only protein with an appreciable sulphur content, a portion of which is present as cysteine, which, as we have shown, reacts readily with iodine. Therefore, only a portion of the iodine number of wool is due to the amino nitrogen content of keratin. Zein and gliadin exhibit high iodine numbers and are reported to have isoelectric points at relatively high pH values.

The experimentally determined iodine numbers of silk, wool, and gelatin are in fair agreement with the calculated values assuming stoichiometric reaction with the amino groups. These values are compared in table 3. Zein (8) is reported to contain no free amino nitrogen and gliadin to contain only 1.9 mgs of amino nitrogen per gram of protein. For these the calculated iodine numbers are much lower than the experimental ones.

TABLE 3.—*Comparison of the experimental iodine number with calculated iodine numbers assuming stoichiometric reaction with the amino groups*

Protein	Amino nitrogen per g protein	Iodine number	
	mg	*Calculated*	*Experimental*
Silk	1.5–1.7 (9)	2.7–3.1	3.7
Wool	5.7 (10)	10.3	[a] 8.3–9.4
Do	9.2 (11)	16.7	
Gelatin	5.5 (12)	9.9	10.2
Zein	0 (12)	0	27.5
Gliadin	1.9 (13)	3.4	25.0

[a] These are corrected values, obtained by subtracting that portion of the iodine number due to reaction with the cysteine group from the iodine number of untreated wool. Reference to table 4 shows that the action of nitrous acid or formaldehyde upon wool lowers the iodine number 8.3 to 9.4 units. Since these reagents may be presumed to react with the free amino groups but not with the cysteine sulphur, the portion of the iodine number of wool due to amino nitrogen appears to be of this order.

TABLE 4.—*Iodine numbers of raw wool and wool treated with various chemical reagents*

Experiment no.	Treatment	Iodine no.
1	Raw wool – scoured with solvents and rinsed	14.2
2	Overscoured – 1 percent soda ash, 70 C	14.2
3	Formaldehyde, 1 percent solution	5.9
4	Neutral H_2O_2, 1 percent solution	14.1
5	NH_2SO_4	7.2
6	Acid H_2O_2, 1 percent solution in NH_2SO_4	7.2
7	Treatment 5, followed by Na_2CO_3 solution	14.2
8	Ammoniacal H_2O_2, 1 percent solution	4.3
9	Alkaline H_2O_2, 1 percent solution (0.5 percent Na_2CO_3)	5.3
10	Acid solution of $KMnO_4$, 1 percent, 8 hours	1.5
11	Solution HNO_2, 0.1 percent, 25 C	4.7
12	Solution HNO_2, 0.1 percent, 0 C	4.8

3. WOOL

Samples of raw wool were treated with various chemical reagents and their iodine numbers were determined, with the results shown in table 4. A comparison of the iodine numbers in experiments 1 and 2 demonstrates that overscouring the wool, for example, by increasing the temperature and the concentration of alkali to such an extent that the wool is damaged in appearance and harshened, does not affect either the content of cysteine sulphur or of amino nitrogen.

In the neutral solution (experiment 4) hydrogen peroxide does not affect the iodine number. In the acid solution (experiment 6) peroxide has the same effect as that produced by the acid alone under the same conditions (experiment 5) and this effect is entirely removed by neutralization (experiment 7). In contrast, the alkaline peroxide solutions (experiments 8 and 9) lower the iodine number to a marked degree. These results indicate that in neutral and acid solutions hydrogen peroxide oxidizes neither the cysteine sulphur nor the amino groups in wool, while in alkaline solutions, hydrogen peroxide apparently attacks both groups to a limited extent.

A stronger oxidizing agent, potassium permanganate (experiment 10) lowers the iodine number to a greater degree than any other reagent used, but the wool is severely damaged by this treatment.

A solution of nitrous acid would be expected to lower the iodine number of wool by converting amino groups to hydroxyl groups. Nitrous acid may also oxidize the cysteine sulphur in wool. The iodine numbers in experiments 11 and 12 in table 3 were obtained after 3 hours' treatment with 0.1 percent solutions of nitrous acid. Higher concentrations or longer treatments do not produce appreciably lower iodine numbers, but cause an increased yellowing of the wool, especially at temperatures above 0 C.

While acid lowers the iodine number, as already pointed out, if it is removed by an alkaline treatment the iodine number returns to the original value. This complete neutralization or removal of combined acid is accomplished only by soaking the acid-treated wool for a considerable time in an excess of the alkaline solution. Merely titrating rapidly to the phenolphthalein and point does not remove all of the combined acid. The evidence that a definite amount of acid combines chemically with wool and cannot be removed by mere

rinsing with water is illustrated in figure 1. Here it is shown that prolonged rinsing alone removes only a portion of the acid, while all the acid remaining on the wool may be readily removed by neutralization, after which the iodine number of the wool returns to its original value. Since it has been shown that the iodine number bears an inverse relationship to the amount of acid on the wool, the minimum difference between the curves may be taken as a measure of the chemically combined acid in the unneutralized wool.

It is well known that strong alkalis, even in very dilute solution, have an injurious action upon wool and that somewhat more concentrated solutions will destroy the wool fibers, dissolving or dispersing and hydrolyzing the keratin. Figure 2 illustrates the effects upon the iodine number and upon the amino nitrogen content of wool resulting from the action of 0.5 normal sodium hydroxide solution at

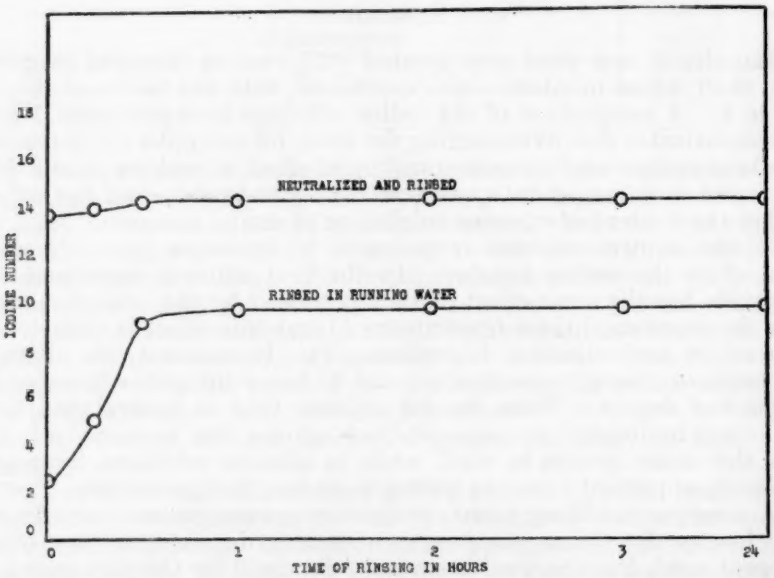

FIGURE 1.—*The effects of (a) rinsing, and (b) neutralizing plus rinsing of wool previously soaked in normal sulphuric acid, as shown by the iodine numbers.*

38 C. Separate one-gram samples of wool were treated with 100 ml of 0.5 normal sodium hydroxide solution for each test. At the time intervals indicated two samples were neutralized with acetic acid. One was evaporated to dryness at 60 C under reduced pressure and the iodine number of the residue was determined. The amino nitrogen content of the other sample was determined by the Van Slyke method. Although the wool fibers appear to be dissolved in the sodium hydroxide solution at the end of 2 hours, the results of the Van Slyke analysis show that only partial hydrolysis of the wool has been accomplished even at the end of 36 hours. The iodine number rises rapidly during the first hour and becomes constant after 8 hours. The results show that the determination of the iodine number is not a measure of the hydrolytic breakdown of wool.

The examples and suggestions given above show the applicability of the method for a number of purposes. Further study may increase the accuracy and utility of the method.

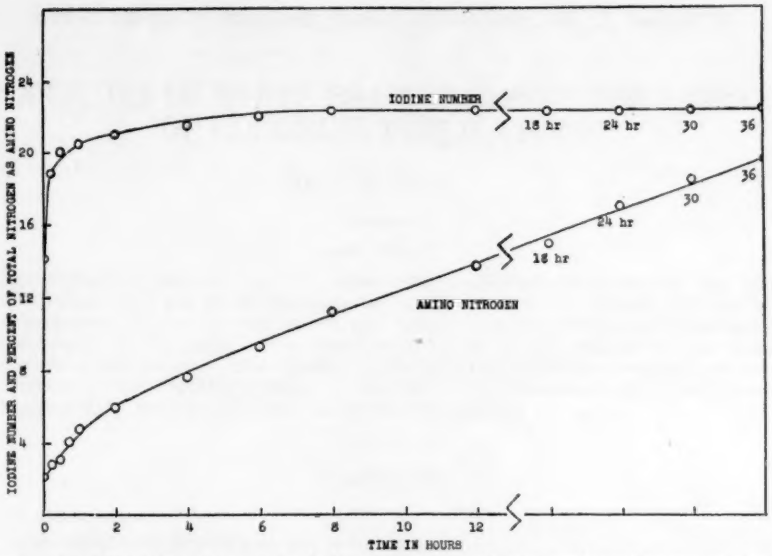

FIGURE 2.—*The effects upon the iodine number and free amino nitrogen content of wool produced by continued action of 0.5 normal sodium hydroxide solution at 38 C.*

IV. REFERENCES

1. Methods of Analysis of the Association of Official Agricultural Chemists, 3d edition, p. 73.
2. C. C. Lucas and E. J. King, the Iodimetric Titration of Cysteine and Allied Substances, Biochem. Jour., vol. 26, p. 2076, 1932.
3. H. Phillips, The Formation and Constitution of Protein Salts From the Standpoint of Modern Theories of Valency, Jour. Intl. Soc. Leather Trade Chemists, vol. 17, pp. 151–165, 1933.
4. A. P. Mathews, Physiological Chemistry, pp. 122–123, 1916, Wm. Wood & Company.
5. M. Harris, The Isoelectric Point of Silk, B.S.Jour. Research, vol. 9, pp. 557–560, 1932.
6. M. Harris, The Isoelectric Point of Wool, B.S.Jour. Research, vol. 8, pp. 779–786, 1932.
7. L. Michaelis and Grineff. Naturwissenschaften, vol. 18, p. 447, 1930.
8. F. A. Csonka, J. C. Murphy, and D. B. Jones, The Isoelectric Points of Various Proteins, Jour. Am. Chem. Soc., vol. 48, pp. 763–768, 1926.
9. M. Harris – Unpublished report.
10. Meunier and Rey, Sur les Proprietes de la Laine, Jour. Soc. Leather Trade Chemists, vol. 11, p. 508, 1927.
11. J. B. Speakman and M. C. Hirst, The Constitution of the Keratin Molecule, Trans. Faraday Soc., vol. 29, pp. 148–164, 1933.
12. D. D. Van Slyke and F. J. Birchard, Jour. Biol. Chem., vol. 16, p. 539, 1931.

WASHINGTON, April 3, 1934.

U.S. Department of Commerce Bureau of Standards

RESEARCH PAPER RP690

Part of Bureau of Standards Journal of Research, vol. 12, June 1934

PROPERTIES OF WHITE BRAILLE PAPERS FOR LIBRARY OF CONGRESS PUBLICATIONS

By C. G. Weber

ABSTRACT

Representative papers used by commercial publishers of books for the blind were studied, and the relationship between quality of the raised dots forming the characters for reading by touch and paper characteristics was determined. The strength of the raised dots was found to be closely related to the tensile properties of the paper. The density of the paper is very important, because of its relation to the reading quality of the dots. Requirements of paper suitable for high-quality Braille publications are recommended.

CONTENTS

		Page
I.	Introduction	811
II.	Description of Braille process printing	812
III.	Description and properties of Braille papers studied	812
IV.	Paper requirements for uniform, high quality-printing	815

I. INTRODUCTION

Braille papers were studied for the purpose of assisting the Library of Congress in the purchase of books for the blind. At the time the study was initiated, many types of papers were in use by Braille printers and current publications did not all have the quality of printing desired for Library of Congress publications. Since no accurate information on the relation of paper properties to quality of printing was available, the establishment of a quality standard required considerable study of the wide variety of papers in use, and correlation of paper characteristics with quality of printing. Books for the blind require paper with certain properties not essential in the case of papers for ink printing. In addition to sufficient strength to resist wear incidental to handling, this paper must permit the embossing of raised dots that are strong enough to resist deformation under the readers' fingers, and free from surface cracks or other harshness that might be irritating to the sensitive touch of the blind readers.

II. DESCRIPTION OF BRAILLE PROCESS PRINTING

Braille process printing is a system of printing for the blind in which points or dots, raised above the surface of the paper, form characters which are read by touch. The processes of printing books and magazines for the blind in commercial Braille presses are generally classified under the two headings, wet printing and dry printing.

Dry printing, as the name implies, is done on the dry paper, and the resulting dots are generally considered unsuitable for books of permanent value. The use of this process is generally confined to magazines of a temporary nature. Since this class of publications is not purchased by the Library of Congress, papers for dry printing were not included in this study.

In wet-process Braille printing, the raised dots forming the characters are formed by embossing wet paper. The paper is prepared for printing by moistening it with water and allowing it to stand in covered piles until the moisture is uniformly distributed. After moistening, the paper is printed on platen presses using embossed plates, and subsequently dried in racks.

III. DESCRIPTION AND PROPERTIES OF BRAILLE PAPERS STUDIED

In order to obtain information on the relation of paper characteristics to the quality of the dots forming the printed characters, both printed and unprinted specimens of the papers used by a number of the leading Braille publishers were studied. The papers were somewhat comparable to commercial ledger papers in weight and quality. However, glue or starch surface sizing used extensively on ledger papers is not used on Braille papers because the surface sizing causes difficulty in wet process printing. The unprinted papers were tested for weight, thickness, bursting strength, folding endurance, tensile properties, ash, degree of sizing, and fiber composition by standard methods.[1] The dots on printed specimens were tested for strength as indicated by resistance to crushing, and they were inspected for surface cracks and other imperfections. The resistance to crushing was determined by measuring, with a dial micrometer, the actual deformation caused by 100 gram deadweight loads on individual dots.

The data for the unprinted and printed papers are given in table 1.

[1] Paper Testing Methods, Technical Association of the Pulp and Paper Industry, 122 E. 42d Street, New York, N.Y.

TABLE 1.—*Test data for Braille papers*

Sample no.[1]	Weight 25 by 40, 500	Thickness	Bursting strength	Folding endurance[3]		Tensile properties[4]				Ash	Water resistance; dry-indicator method	Deformation of dots, 100-g load	Fibers				
						Breaking load		Elongation at rupture[4]					Rag	Chemical wood		Ground wood	Kraft
				Machine	Cross	Machine	Cross	Machine	Cross					Bleached	Unbleached		
	Lb	*In.*	*Points*[2]	*Double folds*[5]	*Double folds*[5]	*kg*	*kg*	*Percent*	*Percent*	*Percent*	*Sec.*	*In.*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
1	96	0.0062	44	14	26	10.1	5.9	2.5	5.5	0.5	52	0.0025	30	70			
2	113	.0063	39	43	100	11.4	4.5	2.0	5.5	7.5	39	.0051	5	65	25	5	
3	96	.0055	37	17	15	9.7	5.1	2.0	4.0	5.0	34	.0044		10	70		20
4	89	.0063	25	31	17	6.8	3.7	1.5	4.0	10.0	22	.0072		100			
5	80	.0052	33	17	75	8.0	4.8	1.5	5.0	2.5	33	.0083		100			
6	85	.0058	37	650	130	9.5	4.7	2.0	4.5	4.5	33	.0047		100			
7	76	.0048	36	75	65	9.2	4.5	1.5	5.5	.5	43	.0068		100			
8	82	.0057	36	940	175	8.9	4.6	1.5	3.0	6.5	30	.0080		100			
9	131	.0070	37	815	730	10.1	7.5	1.5	4.0	4.5	58	.0065		10	80	5	5
10	85	.0052	32	285	55	8.0	4.1	2.5	6.0	.5	23	.0056		100			
11	98	.0064	42	515	270	10.2	6.4	2.0	5.0	5.5	30	.0037		15	70		15
12	80	.0054		2,000	1,000	12.7	6.8	3.0	7.0			.0055		100			
13	77	.0054		750	1,000	9.9	6.5	2.5	6.5			.0063		100			
14	96	.0065		550	58	10.8	4.6	2.5	4.5			.0050		100			

[1] The sizing material in all samples was rosin only.
[2] Bursting pressure in lb/in.[2] through a circular orifice 1.2 inches in diameter.
[3] For test specimen 15 mm wide and 90 mm between jaws.
[4] For test specimens 15 mm wide and 100 mm between jaws.
[5] Results expressed to two significant figures.

The tensile properties of the paper appeared to be the only strength properties closely related to the strength of the embossed dots. Papers of this type are characterized by a distinct grain, resulting in large directional differences in strength. The tensile breaking strength is much higher in the machine direction than in the cross direction, and the stretch, or elongation at rupture, is higher in the cross direction. The strength of the dots is obviously limited by the minimum values; hence by machine-direction elongation and cross-direction tensile breaking strength.

Elongation is apparently of first importance because dot formation requires considerable paper stretch, and failure to perform satisfactorily in this respect results in cracks which impair not only strength, but reading quality. Printing made up of dots that were deformed not more than 0.0050 inch under 100-gram load withstood handling extremely well. Hence it appears essential to require tensile properties high enough to ensure dot deformation of not over 0.0050 inch. From the data in table 1, it will be observed that this desired dot strength was not obtained in papers having cross direction tensile breaking strength of less than 4.5 kg or machine direction elongation of less than 2.0 percent, hence these appeared to be minimum requirements. Machine direction tensile breaking strength and cross direction elongation are important with respect to handling and binding requirements, and minimum values of 9.0 kg and 4.0 percent respectively were considered desirable.

Inasmuch as a thickness of 0.0060 inch is regarded by commercial printers as most satisfactory for the average Braille press, that thickness was selected as standard. Of the papers that conformed closely to that thickness, those weighing approximately 85 pounds per ream (25 by 40 inches, 500 sheets) apparently had the best dots. Lower weights resulted in dots with poor strength, and higher weights were associated with dots with harsh and broken surfaces. Apparently the density of the paper, that is, the ratio of weight to thickness is important, and weight and thickness must both be closely controlled for satisfactory results in printing.

The validity of these findings was checked by testing additional papers. For this purpose, four papers with like fiber composition and comparable tensile properties, but varying somewhat with respect to ratio of weight to thickness, were selected and studied. These papers were tested for weight, thickness, and tensile properties. Printed specimens were tested for strength of dots, and rated with respect to reading quality of printing by blind readers at the Library of Congress. The results of these tests are given in table 2.

TABLE 2

Sample no.	Weight 25 by 40, 500	Thickness	Tensile properties				Deformation of dots under 100-gram load	Rating by blind readers
			Breaking load		Elongation			
			Machine	Cross	Machine	Cross		
	Lb.	*In.*	*kg*	*kg*	*Percent*	*Percent*	*In.*	
1A	85	0.0057	11.3	4.9	2.5	5.0	0.0043	Good.
2A	90	.0052	11.4	5.7	2.0	6.0	.0058	Poor.
3A	78	.0054	10.3	6.6	2.1	5.6	.0044	Do.
4A	85	.0058	9.5	4.7	2.0	4.5	.0047	Preferred.

These results emphasize the importance of the proper weight-thickness relationship. All of the papers had satisfactory strength and dots of high resistance to crushing; however, only two of the papers, 4A and 1A, had dots satisfactory from a standpoint of reading quality. These two papers conformed to within a reasonable tolerance of the standard thickness of 0.0060 inch, and each weighed 85 pounds per ream. The other two papers differed somewhat from 4A and 1A as regards weight and thickness, and the dots of printed specimens had inferior reading surfaces. With these results in addition to the data given in table 1 as a basis, requirements for a white Braille paper suitable for use in the high-quality books for the blind desired by the Library of Congress were recommended.

IV. REQUIREMENTS FOR UNIFORM, HIGH-QUALITY PRINTING

The paper required for wet process Braille printing for use in publications for the Library of Congress resembles a sulphite ledger, machine finish without surface sizing. From a consideration of all of the results, it appears that a paper of that type, having the properties shown in table 3, will be suitable for durable Braille publications of high quality.

TABLE 3

Weight 25 by 40, 500	Thickness	Tensile breaking strength (minimum)		Elongation at rupture (minimum)		Stock	Color
		Machine	Cross	Machine	Cross		
Lb. 85±4	*In.* 0.0060 ±.0005	*kg* 9.0	*kg* 4.5	*Percent* 2.0	*Percent* 4.0	Free from ground wood or unbleached wood fibers.	White.

Three of the papers tested met the requirements (see table 3) in all respects, no. 6 in table 1 and nos. 1A and 4A in table 2. All of those papers were entirely satisfactory as judged by blind readers. Also, paper conforming to the above requirements has been obtained in commercial quantities by a publishing house for use in the publications for the Library of Congress. This paper moistened and printed well, and the quality of dots printed on different presses by different publishers was in all cases entirely satisfactory to blind readers.

WASHINGTON, March 14, 1934.

INDEX TO VOLUME 12

A

Page

Absolute determination of the ampere, RP685 665
Absorption spectrum of tantalum, RP671 459
Acetates, alkali zinc uranyl, properties of, RP672 471
Acken, J. S., Some physical properties of platinum-rhodium alloys, RP650 249
Acree, S. F., Harry Matheson, John O. Burton, and, A glass electrode potentiometer system for the determination of the pH values of weakly buffered solutions such as natural and treated waters, RP634 67
Aerodynamics of tall buildings, RP637 103
Aircraft propeller vibration indicator, RP678 537
Air flow meter for paper testing, RP681 567
Air permeability instrument, RP681 567
Air permeability of paper, RP681 567
Alloy steels, thermal conductivity, RP669 441
Alloys of platinum and rhodium, RP650 249
Alloys, thermal expansion of copper-tin-lead-zinc, RP665 391
Alloys, wear by plastic clay, RP675 501
Aluminum chloride for separating cotton from wool, RP635 75
Amino acids, iodine numbers of, RP689 803
Ampere, absolute determination of, RP685 665
Amplifier, RP663 379
Amplifier, direct current, RP641 167
Amplifier, ultraviolet intensity meter, RP647 231
Analysis of gases {RP643 185 / RP680 551}
Analysis wool-cotton, RP635 75
Analytical separation of Ir, Pd, Rh, Pt, RP655 291
Appel, Wm. D., Herbert F. Schiefer and, Hosiery testing machine, RP679 543
Arc spectrum of tantalum, RP671 459

B

Balance wheels for watches, RP670 451
Beams, properties of brick, RP683 609
Beams, strain measurement of, RP662 363
Bearing bronzes, thermal expansion, RP665 391
Beij, K. Hilding, Flow in roof gutters, RP644 193
Berkner, L. V., D. M. Stuart, S. S. Kirby and, Studies of the ionosphere and their application to radio transmission, RP632 15
Bishop, Dana L., A sedimentation method for the determination of the particle size of finely divided materials, (such as hydrated lime), RP642 173
Black bodies as standards of color temperature, RP677 527
Blood gas, analysis of, RP680 551
Bogue, R. H., Wm. Lerch and, Heat of hydration of portland cement pastes, RP684 645
Bond strength, (mortar to brick), RP683 609
Bower, J. H., Comparative efficiencies of various dehydrating agents used for drying gases (a survey of commercial drying agents), RP649 241
Braille printing papers, RP690 811
Branham, Joseph R., Errors in gas analysis arising from loss of gas by solution in rubber connections and stopcock lubricant, RP661 353
Brass, underground corrosion, RP638 119
Bricks, masonry, RP683 609
Bright, H. A., Determination of small amounts of zinc in steels and irons, RP664 383
Bromide-ion and stability of photographic emulsions, RP646 223
Bronzes, bearing, thermal expansion, RP665 391
Buffers, pH of, RP634 67
Buildings, (roof gutters), RP644 193
Buildings, wind pressure on, RP637 103
Bunting, Elmer N., Edward W. Washburn and, Note on phase equilibria in the system Na_2O-TiO_2, RP648 239
Burton, John O., Harry Matheson, and S. F. Acree, A glass electrode potentiometer system for the determination of the pH values of weakly buffered solutions such as natural and treated waters, RP634 67
Butane, normal, heat of combustion, RP686 735

C

Calcium silicates, reaction of water on, RP687 751
Carbonization of cotton, RP635 75
Carbonization process for wool, RP673 475
Carpets, wear of, RP640 155
Carroll, Burt H., Donald Hubbard, and C. M. Kretchman, The photographic emulsion: Notes on stability of finished plates, RP646 223
—— *and Donald Hubbard*, Kinetics of reaction between silver bromide and photographic sensitizers, RP659 329
Carson, F. T., A sensitive instrument for measuring the air permeability of paper and other sheet materials, RP681 567
—— Effect of experimental conditions on the measurement of air permeability of paper, RP682 587
Cast iron, thermal conductivity, RP669 441
Cast iron, underground corrosion, RP638 119
Cathode-ray oscillograph, RP636 87
Cement chemistry, RP684 645
Cements, masonry, RP683 609
Clay, abrasive action of plastic, RP675 501
Cleveland, Richard S., Herbert F. Schiefer and, Wear of carpets, RP640 155
Coatings, metallic, RP638 119
Coatings, zinc, test of, RP688 785
Coblentz, W. W., and R. Stair, A portable ultraviolet intensity meter, consisting of a balanced amplifier, photoelectric cell, and microammeter, RP647 231
—— and R. Stair, Data on the spectral erythemic reaction of the untanned human skin to ultraviolet radiation, RP631 13
Color of equal-energy stimulus, filters for producing, RP652 263
Color grading, Lovibond red glasses for, RP653 269
Color temperature standards, RP677 527
Composition of glass, RP667 421
Compression cutting tests for rubber, RP674 489
Conductivity, thermal, of irons and steels, RP669 441
Conductivity, thermal, metals, RP668 429
Contrast ratio for paper, RP660 345
Copper sulphate test for zinc coatings, RP688 785
Copper-tin-lead-zinc alloys, thermal expansion, RP665 391
Copper, underground corrosion, RP638 119
Corrosion, underground, RP638 119
Cotton-wool analysis, RP635 75
Crystallography of alkali zinc uranyl acetates, RP672 471
Current balance, An absolute determination of the ampere, RP685 665
Curtis, H. L., and Roger W. Curtis, An absolute determination of the ampere, RP685 665
Curtis, Roger W., H. L. Curtis and, An absolute determination of the ampere, RP685 665

Page

Curtiss, L. F., A gamma-ray ionization chamber for use with a direct current amplifier, RP641 167
—, Portable detector for radium, RP663 379
Cutting tests for rubber, RP674 489

D

Davis-Gibson filters, RP652 263
Davis, Raymond, and K. S. Gibson, Filters for producing the color of the equal-energy stimulus, RP652 263
Dehydrating agents, efficiencies of, RP649 241
Density of liquids, RP656 305
Diatomaceous silica, reaction with lime solutions, RP687 751
Dielectric loss measurements, RP636 87
Dies, wear by plastic clay, RP675 501
Distillation apparatus, RP651 259
Dryden, Hugh L., and L. B. Tuckerman, A propeller-vibration indicator, RP678 537
Drying agents, efficiencies of, RP649 241

E

Electric current—An absolute determination of the ampere, RP685 665
Electrical resistance standards {RP639 147 / RP657 313}
Elinvar hairsprings for watches, RP670 451
Emulsions, photographic {RP646 223 / RP659 329}
Equal-energy stimulus, filters for producing color of, RP652 263
Erythemic reaction to ultraviolet, RP631 13
Ethane, heat of combustion, RP686 735
Expansion of bricks and mortars, RP683 609
Expansion, thermal, of bearing bronzes, RP665 391
Expansion, thermal, of copper-tin-lead-zinc alloys, RP665 391
Expansion, thermal, of glass, RP667 421

F

Failures, fatigue, aircraft propellers, RP678 537
Fatigue failures of aircraft propellers, RP678 537
Fibers, wear of wool, RP640 155
Filters, for producing color of equal-energy stimulus, RP652 263
Finn, A. N., J. C. Young, B. C. Schmid and, Thermal expansions for some soda-lime-silica glasses as functions of the composition, RP667 421
Flint, E. P., and Lansing S. Wells, A study of the system CaO-SiO_2-H_2O at 30 C and of the reaction of water on the anhydrous calcium silicates, RP687 751
Floors, steel, strength of, RP662 363
Fluorescence of oscillograph screen, RP636 87
Forsterite, RP645 215
Fractionating column with fritted glass plates, RP651 259
Freezing metals as fixed points on color temperature scale, RP677 527
Freezing of bricks and mortars, RP683 609
Freezing point of rhodium, RP676 519
Frequencies, ionosphere, RP632 15
Frequency, standard transmitting sets, RP630 1
Frequency standards, radio, RP630 1
Fritz, William C., Harvey A. Neville, Milton Harris and, The iodine number of wool: A method for determining the action of various chemical reagents on wool and other proteins, RP689 803

G

Galvanized coatings, test of, RP688 785
Galvanized pipe, underground corrosion, RP638 119
Gamma-ray ionization chamber, RP641 167
Gas analysis, errors in {RP661 353 / RP680 551}
Gases, dehydrating agents for drying, RP649 241
Gases, permeability of sheet materials to, RP681 567

Page

Gases, purity of, RP643 185
Gases, solubility in rubber, RP661 353
Generator, electric, for indicating propeller vibrations, RP678 537
Gibson, K. S., Raymond Davis and, Filters for producing the color of the equal-energy stimulus, RP652 263
Gilchrist, Raleigh, A method for the separation of ruthenium from platinum, palladium, rhodium, and iridium, RP654 283
—, Methods for the separation of platinum, palladium, rhodium, and iridium from one another and for their gravimetric determination, RP655 291
Glass, composition and temperatures of, RP667 421
Glass electrode circuit, RP634 67
Glass plates, fractionating column with fritted, RP651 259
Glass, thermal expansion of, RP667 421
Glasses, Lovibond red, standardization, RP653 269
Glaze, F. W., Herbert Insley and, Some optical and crystallographical properties of the alkali zinc uranyl acetates, RP672 471
Gould, Ralph E., Comparative performance of watches with elinvar and with steel hairsprings, RP670 451
Gravimetric determination of Ir, Pd, Rh, Pt, RP655 291
Groesbeck, E. C., and H. H. Walkup, Preece test (copper sulfate dip) for zinc coating, RP688 785
Gutters, roof, RP644 193

H

Hairsprings for watches, elinvar and steel, RP670 451
Hardening of cement, RP684 645
Harris, C. L., Influence of neighboring structures on the wind pressure on tall buildings, RP637 103
Harris, Forest K., A new cathode-ray oscillograph and its application to the study of power loss in dielectric materials, RP636 87
Harris, Milton, The carbonization process: A study of the system wool—sulphuric-acid—water, RP673 475
Harris, Milton, Harvey A. Neville, and William C. Fritz, The iodine number of wool: A method for determining the action of various chemical reagents on wool and other proteins, RP689 803
Heat of hydration of portland cement, RP684 645
Heats of combustion of ethane, propane, normal butane, normal pentane, RP686 735
Heindl, R. A., and W. L. Pendergast, Olivine as a refractory, RP645 215
Hidnert, Peter, Thermal expansion of bearing bronzes, RP665 391
Holt, W. L., Compression cutting test for rubber, RP674 489
Hosiery, laundering of, RP679 543
Hosiery, performance test for, RP679 543
Hosiery, skimping of, RP679 543
Hosiery testing machine, RP679 543
Hubbard, Donald, Burt H. Carroll and, Kinetics of reaction between silver bromide and photographic sensitizers, RP659 329
Hubbard, Donald, C. M. Kretchman, B. H. Carroll and, The photographic emulsion: Notes on stability of finished plates, RP646 223
Humidity, effect on paper, RP682 587
Humidity equilibria of paper, RP633 53
Hydration of portland cement, RP684 645
Hydraulics; flow in roof gutters, RP644 193
Hydrogen electrodes, RP634 67
Hydrogen-ion concentration of calcium silicate solutions, RP687 751
Hydrogen-ion concentration, weakly buffered solutions, RP634 67
Hydrogen-ion measurements, RP634 67
Hydrogen-ion and stability of photographic emulsions, RP646 223
Hydrolysis of calcium silicates, RP687 751

I

Page

Ice point, reproducibility, RP658 323
Indicator, propeller-vibration, RP678 537
Insley, Herbert, and Francis W. Glaze, Some optical and crystallographical properties of the alkali zinc uranyl acetates, RP672 471
Insulation, power factor, RP636 87
Iodine number of wool and other proteins, RP689 803
Ionization chamber, RP663 379
Ionization chamber, gamma-ray, RP641 167
Ionosphere frequencies, RP632 15
Iridium, analytical separation of, RP655 291
Iridium, separation of ruthenium from, RP654 283
Iron, malleable, underground corrosion, RP638 119
Iron, thermal conductivity, RP668 429
Iron and steel, thermal conductivity, RP669 441
Irons and steels, zinc in, RP664 383
Isotopic composition of natural waters, RP656 305

J

Jessup, Daniel A., Ralph T. Mease and, Analysis of wool-cotton textiles, RP635 75
Judd, Deane B., Sources of error in measuring opacity of paper by the contrast-ratio method, RP660 345
——, *Wm. F. Roeser, H. T. Wensel and,* Establishment of a scale of color temperature, RP677 527

K

Kennelly-Heaviside layer, RP632 15
Kiess, C. C., and E. Z. Stowell, First spectrum of tantalum, RP671 459
Kirby, S. S., L. V. Berkner, and D. M. Stuart, Studies of the ionosphere and their application to radio transmission, RP632 15
Kretchman, C. M., Donald Hubbard, B. H. Carroll and, The photographic emulsion: Notes on stability of finished plates, RP646 223

L

Laundering of hosiery, RP679 543
Layers of ionosphere, RP632 15
Lead, underground corrosion, RP638 119
Leather, air permeability of, RP681 567
Lerch, Wm., and R. H. Bogue, Heat of hydration of portland cement pastes, RP684 645
Lime-cement mixtures, RP683 609
Lime, effect on properties of masonry mortars, RP683 609
Lime, particle size, RP642 173
Lime-silica-water system at 30 C, RP687 751
Liquids, density, RP656 305
Lithographic papers, RP633 53
Logan, K. H., and R. H. Taylor, Soil corrosion studies, 1932. Rates of loss of weight and pitting of ferrous and nonferrous specimens and metallic protective coatings, RP638 119
Lovibond red glasses, standardization, RP653 269
Lubricants, stopcock, solubility of gases in, RP661 353

M

Magnesite, RP645 215
Magnetism of watches, RP670 451
Malleable iron, underground corrosion, RP638 119
Manometric method of gas analysis, RP680 551
Martin, A. D., L. Mickey and, Development of standard-frequency transmitting sets, RP630 1
Materials, air permeability of sheet, RP681 567
Matheson, Harry, S. F. Acree, John O. Burton and, A glass electrode potentiometer system for the determination of the pH values of weakly buffered solutions, such as natural and treated waters, RP634 67
Mease, Ralph T., and Daniel A. Jessup, Analysis of wool-cotton textiles, RP635 75
Measurements, standard radio-frequency, RP630 1
Melting point of rhodium, RP676 519
Melting points of sodium titanates, RP648 239
Metal dies, wear by plastic clay, RP675 501
Metal pipe, underground corrosion, RP638 119
Metallic protective coatings, RP638 119
Metals, thermal conductivity, RP668 429; RP669 441
Meter, ultraviolet intensity, RP647 231
Mickey, L., and A. D. Martin, Development of standard-frequency transmitting sets, RP630 1
Microammeter in ultraviolet measurements, RP647 231
Moisture content of paper, RP633 53
Mortars, masonry, RP683 609

N

Neville, Harvey A., William C. Fritz, Milton Harris and, The iodine number of wool: A method for determining the action of various chemical reagents on wool and other proteins, RP689 803
Nitrided steel dies, wear by plastic clay, RP675 501

O

Olivine, a refractory, RP645 215
Opacimeter, sources of error, RP660 345
Opacity of paper, RP660 345
Optical properties of alkali zinc uranyl acetates, RP672 471
Oscillators, controlled, RP630 1
Oscillograph, cathode-ray, RP636 87
Osgood, W. R., A. H. Stang, L. B. Tuckerman and, Test of a flat steel-plate floor under loads, RP662 363

P

Palladium, analytical separation of, RP655 291
Palladium, separation of ruthenium from, RP654 283
Palmer, L. A., and D. A. Parsons, A study of the properties of mortars and bricks and their relation to bond, RP683 609
Paper, air permeability of, RP681 567; RP682 587
Paper conditioning, RP633 53
Paper, moisture content and dimensions, RP633 53
Paper, oil-impregnated, power losses, RP636 87
Paper opacity, RP660 345
Papers for blind readers, RP690 811
Papers, lithographic, RP633 53
Parsons, D. A., L. A. Palmer and, A study of the properties of mortars and bricks and their relation to bond, RP683 609
Pendergast, W. L., R. A. Heindl and, Olivine as a refractory, RP645 215
Pentane, normal, heat of combustion, RP686 735
Performance of watches under various conditions, RP670 451
Permeability instrument, air, RP681 567
Permeability of paper to air, RP682 587
Phase equilibria in the system Na_2O–TiO_2, RP648 239
Photoelectric amplifier, ultraviolet intensity meter, RP647 231
Photographic emulsions, RP646 223; RP659 329
Photographic sensitizers, RP659 329
Pipe, underground corrosion, RP638 119
Plates, photographic, RP646 223
Plates, steel, strain measurement of, RP662 363
Platinum, analytical separation of, RP655 291
Platinum-rhodium alloys, RP650 249
Platinum, separation of ruthenium from, RP654 283
Points, fixed, on color temperature scale, RP677 527
Porcelain dies, wear by plastic clay, RP675 501
Portable radium detector, RP663 379
Portland cement, hydration, RP684 645
Portland cement, reaction with water, RP687 751

Page

Potentiometer, glass electrode, RP634 67
Power factor measurements, RP636 87
Preece test for zinc coatings, RP688 785
Pressure of wind on tall buildings, RP637 103
Printing papers, Braille, RP690 811
Propane, heat of combustion, RP686 735
Propeller, aircraft, vibration indicator, RP678 537
Properties of platinum-rhodium alloys, RP650 249
Proteins, iodine number of, RP689 803
Purification of rhodium, RP676 519
Pycnometer for measuring density, RP656 305

R

Radioactivity, measuring, RP641 167
Radiation, ultraviolet, RP647 231
Radiation, ultraviolet, spectral erythemic reaction, RP631 13
Radio-frequency standards, RP630 1
Radio transmission, correlation with vertical incidence, RP632 15
Radium detector, RP663 379
Rate of watches, RP670 451
Ratio of absolute to international ampere, RP685 665
Rectifying column, RP651 259
Refractive index, effect on microscopic measurements of particle size, RP642 173
Refractory, olivine as a special, RP645 215
Resistance standards {RP639 147 / RP657 313}
Resonant vibration of aircraft propellers, RP618 537
Rhodium, analytical separation of, RP655 291
Rhodium, freezing point, RP676 519
Rhodium-platinum alloys, RP650 249
Rhodium, purification, RP676 519
Rhodium, separation of ruthenium from, RP654 283
Roeser, Wm. F., D. B. Judd, H. T. Wensel and, Establishment of a scale of color temperature, RP677 527
——, *and H. T. Wensel,* Freezing point of rhodium, RP676 519
Roof gutters, RP644 193
Rossini, Frederick D., Calorimetric determination of the heats of combustion of ethane, propane, normal butane, and normal pentane, RP686 735
Rubber, cutting and shear tests, RP674 489
Rubber, solubility of gases in, RP661 353
Ruthenium, determination of, RP654 283
Ruthenium, distillation as ruthenium tetroxide, RP654 283
Ruthenium, separation from Ir, Pd, Pt, and Rh, RP654 283

S

Schicktanz, S. T., A fractionating column with fritted glass plates, RP651 259
Schiefer, Herbert F., and Wm. D. Appel, Hosiery testing machine, RP679 543
——, and Richard S. Cleveland, Wear of carpets, RP640 155
Schmid, B. C., A. N. Finn, and J. C. Young, Thermal expansions of some soda-lime-silica glasses as functions of the composition, RP667 421
Sedimentation method for particle size determinations, RP642 173
Sensitizers, photographic, RP659 329
Shear tests for rubber, RP674 489
Shelton, S. M., Thermal conductivity of some irons and steels over the temperature range 100 to 500 C, RP669 441
——, *M. S. Van Dusen and,* Apparatus for measuring thermal conductivity of metals up to 600 C, RP668 429
Shepherd, Martin, A critical test for the purity of gases, RP643 185
——, Significant vapor pressure considerations of the Van Slyke manometric method of gas analysis, RP680 551
Silica, solubility in lime solution, RP687 751
Silicic acid ionization constants, RP687 751

Page

Singer, George, Lauriston S. Taylor and, Standard absorption curves for specifying the quality of X-radiation, RP666 401
Size, particle, determination of, RP642 173
Sizing, removal from cotton-wool, RP635 75
Smith, Edgar, R. Edward W. Washburn and, An examination of water from various natural sources for variations in isotopic composition, RP656 305
Snyder, L. W., and C. G. Weber, Reactions of lithographic papers to variations in humidity and temperature, RP633 53
Sodium titanates, melting points, RP648 239
Soil corrosion, RP638 119
Sorption of masonry mortars, RP683 609
Specification of X-ray quality, RP666 401
Spectra of tantalum, RP671 459
Spectral erythemic reaction, RP631 13
Stability of photographic plates, RP646 223
Stair, R. W., W. W. Coblentz and, A portable ultraviolet intensity meter, consisting of a balanced amplifier, photoelectric cell, and microammeter, RP647 231
——, *W. W. Coblentz and,* Data on the spectral erythemic reaction of the untanned human skin to ultraviolet radiation, RP631 13
Standard radio-frequency transmissions, RP630 1
Standards of color temperature, RP677 527
Standards of resistance, RP657 313
Standards of resistance, temperature coefficient, RP639 147
Standards, X-ray, RP666 401
Stang, A. H., W. R. Osgood, L. B. Tuckerman and, Test of a flat steel-plate floor under loads, RP662 363
Steel floors, strain measurement, RP662 363
Steel plates, strength of, RP662 363
Steel, thermal conductivity, RP668 429
Steel, underground corrosion, RP638 119
Steels and irons, zinc in, RP664 383
Steels, stainless, thermal conductivity, RP669 441
Still with fritted glass plates, RP651 259
Stowell, E. Z., C. C. Kiess and, First spectrum of tantalum, RP671 459
Strain measurement, steel floors, RP662 363
Strength, compressive, of bricks, mortars, and brick-mortar assemblages, RP683 609
Stuart, D. M., L. V. Berkner, S. S. Kirby and, Studies of the ionosphere and their application to radio transmission, RP632 15
Stull R. T., Wear of dies for extruding plastic clay, RP675 501
Sulphuric acid in wool and water, RP673 475

T

Tantalum wave lengths, RP671 459
Taylor, Lauriston S., and George Singer, Standard absorption curves for specifying the quality of X-radiation, RP666 401
Taylor, R. H., K. H. Logan and, Soil corrosion studies, 1932. Rates of loss of weight and pitting of ferrous and non-ferrous specimens and metallic protective coatings, RP638 119
Temperature coefficient of resistance standards, RP639 147
Temperature, color, RP677 527
Temperature, effect on air permeability measurements, RP682 587
Temperature, effect on lithographic papers, RP633 53
Temperature, effect on watches, RP670 451
Temperature of freezing rhodium, RP676 519
Temperature of glass, RP667 421
Testing air permeability of sheet materials, RP681 567
Test of zinc coatings, RP688 785
Textiles, wool-cotton analysis, RP635 75
Thermal conductivity of metals, RP668 429
Thermal conductivity of some irons and steels, RP669 441
Thermal expansion, bearing bronzes, RP665 391
Thermal expansion of copper-tin-lead-zinc alloys, RP665 391
Thermal expansion of glass, RP667 421

	Page
Thermal reactions of portland cement, RP684	645
Thomas, James L., Frank Wenner and, A method of adjusting the temperature coefficient and resistance of low-valued resistance standards, RP639	147
——, Reproducibility of the ice point, RP658	323
——, Some experiments with pure-metal resistance standards, RP657	313
Timepieces, magnetism of, RP670	451
Tintometer red glasses, calibration, RP653	269
Titanates of sodium, melting points, RP648	239
Titanium dioxide, phase equilibria, RP648	239
Translucency of paper, RP660	345
Triple point of water, RP658	323
Tuckerman, L. B., Hugh L. Dryden and, A propeller-vibration indicator, RP678	537
——, *A. H. Stang and W. R. Osgood,* Test of a flat steel-plate floor under loads, RP662	363
Twisting moment of tall buildings, RP637	103

U

Ultraviolet dosage intensity meter, RP647	231
Ultraviolet erythemic reaction, PR631	13
Underground corrosion, RP638	119
Units, electrical; the ampere, RP685	665
Uranyl acetates, properties of, RP672	471

V

Van Dusen, M. S., and C. M. Shelton, Apparatus for measuring thermal conductivity of metals up to 600 C., RP668	429
Van Slyke method of gas analysis, RP680	551
Vibration of aircraft propellers, RP678	537
Volume changes in masonry mortars, RP683	609

W

Walker, Geraldine K., Statistical investigation of the Uniformity of grades of 1,000 Lovibond red glasses, RP653	269
Walkup, H. H., E. C. Groesbeck and, Preece test (copper sulfate dip) for zinc coating, RP688	785
Washburn, Edward W., and Elmer N. Bunting, Note on phase equilibria in the system Na_2O–TiO_2, RP648	239
——, *and Edgar R. Smith,* An examination of water from various natural sources for variations in isotopic composition, RP656	305
Watches with elinvar hairsprings, RP670	451
Water, hydrogen-ion concentration, RP634	67
Water, ice point of, RP658	323
Water retaining capacity of mortars, RP683	609
Waters, natural, isotopic composition of, RP656	305
Wear of carpets, RP640	155
Weber, C. G., Properties of white Braille papers for Library of Congress publications, RP690	811
Weber, C. G., L. W. Snyder and, Reactions of lithographic papers to variations in humidity and temperature, RP633	53
Weighing device, automatic recording, RP642	173
Welded steel floors, RP662	363
Wells, Lansing S., E. P. Flint and, A study of the system CaO–SiO_2–H_2O at 30 C and of the reaction of water on the anhydrous calcium silicates, RP687	751
Wenner, Frank, and James L. Thomas, A method of adjusting the temperature coefficient and resistance of low-valued resistance standards, RP639	147
Wensel, H. T., Wm. F. Roeser and, Freezing point of rhodium, RP676	519
——, *D. B. Judd, and Wm. Roeser,* Establishment of a scale of color temperature, RP677	527
Willemite, fluorescence of, RP636	87
Wind pressure on tall buildings, RP637	103
Wool-cotton, analysis, RP635	75
Wool, deterioration of, RP673	475
Wool fibers, wear of, RP640	155
Wool, iodine number of, RP689	803
Wool, sulphuric acid absorption, RP635	75
Wool—sulphuric-acid—water system, RP673	475
Wool treated with various chemical reagents, RP689	803
Wrought iron, underground corrosion, RP638	119

X

X-ray, absorption, RP666	401
X-ray, standards, RP666	401

Y

Young, J. C., A. N. Finn, B. C. Schmid and, Thermal expansions of some soda-lime-silica glasses as functions of the composition, RP667	421

Z

Zinc coatings, test of, RP688	785
Zinc in steels and irons, RP664	385
Zinc uranyl acetates, properties of, RP672	471